



Arnold Schwarzenegger  
Governor

# COOLING TOWER WATER QUALITY PARAMETERS FOR DEGRADED WATER

*Prepared For:*  
**California Energy Commission**  
Public Interest Energy Research Program

*Prepared By:*  
**Michael N. DiFilippo, Consultant**

**PIER FINAL PROJECT REPORT**

April 2006  
CEC-500-2005-170



***Prepared By:***

Michael N. DiFilippo, Consultant  
Berkeley, California

Contract No. 100-98-001

***Prepared For:***

**California Energy Commission**

Public Interest Energy Research (PIER) Program

Joe O'Hagan,

***Contract Manager***

Kelly Birkinshaw,

***Program Area Team Lead***

***Energy-Related Environmental Research***

Martha Krebs, Ph.D.,

***Deputy Director***

**ENERGY RESEARCH AND DEVELOPMENT  
DIVISION**

B. B. Blevins

***Executive Director***

**DISCLAIMER**

This report was prepared as the result of work sponsored by the California Energy Commission. It does not necessarily represent the views of the Energy Commission, its employees or the State of California. The Energy Commission, the State of California, its employees, contractors and subcontractors make no warrant, express or implied, and assume no legal liability for the information in this report; nor does any party represent that the uses of this information will not infringe upon privately owned rights. This report has not been approved or disapproved by the California Energy Commission nor has the California Energy Commission passed upon the accuracy or adequacy of the information in this report.

Please cite this report as follows:

DiFilippo, Michael. 2006. *Cooling Tower Water Quality Parameters for Degraded Water*. California Energy Commission, PIER Energy-Related Environmental Research. CEC-500-2005-170.

## Preface

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Energy Commission), annually awards up to \$62 million to conduct the most promising public interest energy research by partnering with research, development, and demonstration (RD&D) organizations, including individuals, businesses, utilities, and public or private research institutions.

PIER funding efforts are focused on the following RD&D program areas:

- Buildings End-Use Energy Efficiency
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies

*Cooling Tower Water Quality Parameters for Degraded Water* is the final report for contract number 100-98-001, conducted by Michael N. DiFilippo. The information from this project contributes to PIER's Energy-Related Environmental Research program.

For more information on the PIER Program, please visit the Energy Commission's website at [www.energy.ca.gov/pier](http://www.energy.ca.gov/pier) or contact the Energy Commission at (916) 654-5164.

## Table of Contents

Preface.....	ii
Abstract .....	viii
Executive Summary .....	1
1.0 Introduction.....	4
1.1 Report Organization .....	4
2.0 Indices and Guidelines .....	6
2.1 Introduction .....	6
2.2 Simple Indices.....	6
2.2.1 Langelier Saturation Index .....	6
2.2.2 Ryznar Stability Index .....	8
2.2.3 Practical Scaling Index .....	10
2.2.4 Concentration Guidelines .....	10
3.0 Ion Chemistry .....	13
3.1 Introduction .....	13
3.2 Ionic Strength and Activity Coefficients .....	13
3.3 Ion Association .....	16
3.4 Saturation Concentrations of Precipitants.....	21
4.0 Software .....	24
4.1 Introduction .....	24
4.2 State of the Art.....	24
4.3 General Calculation Approach.....	24
5.0 Specialty Chemicals .....	27
5.1 Introduction .....	27
5.2 Scale Control .....	27
5.2.1 Threshold Scale Inhibitors .....	27
5.2.2 Polymer Dispersants.....	30
5.3 Corrosion Control .....	31
5.3.1 Mild Steel Corrosion.....	33
5.3.2 Copper Corrosion .....	35
6.0 Source Water Chemistry.....	37
6.1 Introduction .....	37
6.2 CaCO <sub>3</sub> Molar Equivalents .....	37
6.3 Preparing Source Water Chemistry.....	38
6.3.1 Formatting Source Water Chemistry .....	39

6.3.2.	Alkalinity Speciation .....	40
6.3.3.	Ammonia Speciation .....	43
6.3.4.	Phosphate Speciation.....	45
6.3.5.	Other Concentration Conversions .....	48
6.3.6.	Balancing the Data .....	49
6.3.7.	Finalizing the Data.....	52
7.0	Site-Specific Analysis .....	54
7.1.	Introduction .....	54
7.2.	Develop Cycles-of-Concentration Scenarios .....	55
7.2.1.	Preliminary Cooling Tower Chemistry .....	56
7.2.2.	Speciation .....	56
7.2.3.	Ammonia Speciation .....	56
7.2.4.	Alkalinity Speciation .....	58
7.2.5.	Determining the Sulfate Concentration .....	61
7.2.6.	Phosphate Speciation.....	62
7.2.7.	Summarize the Cycles-of-Concentration Scenarios Data.....	62
7.3.	Ion Association and Ion Activity .....	67
7.3.1.	Calcium and Magnesium Sulfate Ion Association Analysis .....	67
7.3.2.	Ion Association .....	69
7.3.3.	Ion Activity .....	72
7.3.4.	Relative Solubility of Scale-Forming Compounds .....	75
7.3.5.	Burden of Scale-Forming Compounds .....	82
7.4.	Summarizing the Data.....	86
7.5.	Comparing Results to Indices and Standards .....	87
7.6.	Interpreting the Results.....	90
8.0	Water Quality Calculator .....	91
8.1.	Introduction .....	91
8.2.	Loading the Water Quality Calculator .....	91
8.3.	Spreadsheet Arrangement .....	91
8.4.	Entering Data .....	92
8.5.	Data Output .....	92
8.6.	Using the Water Quality Calculator .....	93
8.7.	Analysis of the Sample Source Water Data .....	94
9.0	References.....	101
10.0	Glossary .....	103

## List of Figures

Figure 2-1. Rynzar Index Graph of Scaling and Corrosion Effects .....	9
Figure 3-1. Ionic Strength vs $\text{TDS}_{\text{ion}}$ .....	16
Figure 3-2. Activity Coefficient vs $\text{TDS}_{\text{ion}}$ .....	17
Figure 3-3. Variations in alkalinity, silica, phosphate, sulfide, boron, and ammonia species .....	22
Figure 3-4. $\text{CaSO}_4$ Solubility vs Temperature .....	23
Figure 4-1. Generalized Calculation Procedure .....	26
Figure 5-1. Dispersant Polymer-Crystal Interaction .....	33
Figure 5-2. Sodium polyphosphate and the calcium-polyphosphate complex .....	35
Figure 5-3. The tolyltriazol protective film mechanism .....	36
Figure 6-1. Carbonate Alkalinity Molar Fractions vs pH .....	41
Figure 6-2. $\text{CO}_3^{2-}$ Molar Fraction vs TDS and pH .....	42
Figure 6-3. $\text{CO}_2$ Molar Fraction vs TDS and pH .....	43
Figure 6-4. Ammonia Molar Fractions vs pH .....	44
Figure 6-5. $\text{NH}_3$ Molar Fraction vs pH .....	44
Figure 6-6. Phosphate Molar Fractions vs pH .....	46
Figure 6-7. $\text{H}_3\text{PO}_4$ Molar Fraction vs TDS and pH .....	46
Figure 6-8. $\text{H}_2\text{PO}_4^{-1}$ Molar Fraction vs TDS and pH .....	47
Figure 6-9. $\text{PO}_4^{-3}$ Molar Fraction vs TDS and pH .....	47
Figure 7-1. Cooling Tower Chemistry Evaluation Methodology .....	55
Figure 7-2. $\text{NH}_3$ Molar Fraction vs pH .....	57
Figure 7-3. $\text{CO}_3^{2-}$ Molar Fraction vs TDS and pH .....	59
Figure 7-4. $\text{CO}_2$ Molar Fraction vs TDS and pH .....	59
Figure 7-5. $\text{H}_3\text{PO}_4$ Molar Fraction vs TDS and pH .....	64
Figure 7-6. $\text{H}_2\text{PO}_4^{-1}$ Molar Fraction vs TDS and pH .....	64
Figure 7-7. $\text{PO}_4^{-3}$ Molar Fraction vs TDS and pH .....	65
Figure 7-8. Free $\text{SO}_4^{2-}$ vs $[(\text{Ca}^{+2} + \text{Mg}^{+2})/\text{SO}_4^{2-}]\text{Total}$ , Broad Range .....	70
Figure 7-9. Free $\text{SO}_4^{2-}$ vs $[(\text{Ca}^{+2} + \text{Mg}^{+2})/\text{SO}_4^{2-}]\text{Total}$ , Low Range .....	70

Figure 7-10. OH <sup>-1</sup> vs pH vs TDS, pH=6.5 to 7.5, Temperature=135°F .....	74
Figure 7-11. OH <sup>-1</sup> vs pH vs TDS, pH=7.5 to 8.5, Temperature=135°F .....	74
Figure 7-12. Activity Coefficient vs TDS <sub>ion</sub> .....	75
Figure 7-13. CaCO <sub>3</sub> Solubility vs Temperature .....	77
Figure 7-14. CaSO <sub>4</sub> Solubility vs Temperature .....	77
Figure 7-15. CaHPO <sub>4</sub> Solubility vs Temperature .....	78
Figure 7-16. Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> Solubility vs Temperature .....	78
Figure 7-17. Mg <sub>2</sub> Si <sub>3</sub> O <sub>8</sub> -3.5H <sub>2</sub> O Solubility vs Temperature .....	79
Figure 7-18. SiO <sub>2</sub> Solubility vs Temperature .....	80
Figure 8-1. Example Relative Saturation worksheet .....	99
Figure 8-2. Example Ca Salts-SiO <sub>2</sub> Burden worksheet .....	99
Figure 8-3. Example Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> Mg <sub>2</sub> Si <sub>3</sub> O <sub>8</sub> -3.5H <sub>2</sub> O .....	100
Figure 8-4. Example Total Burden-SiO <sub>2</sub> -LSI worksheet .....	100

## List of Tables

Table 2-1. Water Quality Parameters for Cooling Towers .....	11
Table 3-1. Activity Coefficient Calculation .....	15
Table 3-2. Typical Cations and Anions Involved in Ion Association Analysis .....	20
Table 5-1. Common Phosphonate Threshold Inhibitors .....	28
Table 5-2. Common Dispersants .....	32
Table 6-1. Common CaCO <sub>3</sub> Conversion Factors .....	38
Table 6-2. Source Water Chemistry—Reported Data .....	40
Table 6-3. Source Water Chemistry—Speciation and Electroneutrality Check .....	51
Table 6-4. Source Water Chemistry—Speciated and Balanced .....	53
Table 7-1. Cycle-of-Concentration Scenarios .....	66
Table 7-2. Relative Solubility of Scale-Forming Compounds .....	81



Table 7-3. Burden of Scale-Forming Compounds .....	85
Table 7-4. Data Summary.....	86
Table 7-5. Site-Specific Analysis Comparisons to Indices and Guidelines .....	89
Table 8-1. Example Data Input worksheet .....	95
Table 8-2. Example of the “Default Summary” portion of the Data Input worksheet.....	96
Table 8-3. Example Bal-Spec Source worksheet.....	97
Table 8-4. Example Analysis Summary worksheet.....	98

## Worksheets

Carbonate Alkalinity Speciation Worksheet.....	42
Ammonia Speciation Worksheet .....	45
Phosphate Speciation Worksheet.....	48
Miscellaneous Conversions Worksheet .....	48
Electroneutrality Calculation.....	50
Ammonia Calculation Worksheet .....	57
Alkalinity Calculation Worksheet .....	60
Sulfate Calculation Worksheet.....	62
Phosphate Calculation Worksheet.....	63
Ion Association Worksheet.....	71
Ion Activity Worksheet .....	73

## Abstract

There is a significant amount of pressure to utilize degraded water sources (non-potable water) for cooling for new power plants and repowering projects. Degraded water is more difficult to use, because it usually contains constituents of concern that create problems in cooling systems. Many viable degraded water sources are eliminated from consideration, because the standard evaluation approach is overly simplistic and conservative. Water quality criteria for industrial cooling towers is in the form of simple indices, and general guidelines have been employed for a number of years. Many waters deemed unusable by the standard criteria are usable when evaluated with more sophisticated analytical tools.

This project developed a methodology to evaluate source waters intended for power plant cooling systems, establishing site-specific water quality criteria for degraded water and potable water. The report, *Cooling Tower Water Quality Parameters for Degraded Water*, covers the following related areas:

- The evolution of simple indices and the use of generalized guidelines for water quality criteria for cooling towers
- The chemistry of ion interaction and a more technical approach to developing water quality criteria
- Commercial software, and how it works
- The use of specialty chemicals to extend solubility criteria
- Source water data preparation
- Developing site-specific water quality criteria for cooling towers

Also, a water quality calculator in the form an Excel spreadsheet is provided. The calculator utilizes the methodologies developed in the report to develop site-specific water quality criteria easily and accurately.

Considerations such as source water pretreatment, cooling system materials of construction, and zero liquid discharge strategies are not discussed.

# **Executive Summary**

## **Introduction**

There is a significant amount of pressure to utilize degraded water sources (non-potable water) for cooling for new power plants and repowering projects. Degraded water, by its very nature, is more difficult to use, because it usually contains constituents of concern that create problems in cooling systems. Many viable degraded water sources are eliminated from consideration, because the standard evaluation approach is overly simplistic and conservative. Water quality criteria for industrial cooling towers in the form of simple indices and general guidelines have been employed for a number of years. Many waters deemed unusable by the standard criteria are usable when evaluated with more sophisticated analytical tools.

## **Purpose**

This project's purpose was to develop a methodology to establish site-specific water quality criteria for degraded water and potable water.

## **Project Objectives**

The project focused on the following related areas:

- The evolution of simple indices and the use of generalized guidelines for water quality criteria for cooling towers
- The chemistry of ion interaction and a more technical approach to developing water quality criteria
- Commercial software, and how it works
- The use of specialty chemicals to extend solubility criteria
- Source water data preparation
- Developing site-specific water quality criteria for cooling towers

## **Outcomes**

Predicting the solubility of sparingly soluble salts (such as calcium carbonate) in water has been a concern of municipal, commercial, and industrial system operators for many years. In the early 1900s, research into the effects of ion interaction of scaling salts was just being quantified and studied. Later, indices were developed to predict the behavior of calcium carbonate to protect water distribution systems from scale and corrosion. Water quality standards have since evolved for cooling systems that incorporate indices and concentration guidelines for scaling constituents such as calcium carbonate, calcium sulfate, and silica. This report contains a discussion of the derivation and use of simple calcium carbonate prediction indices and the current convention for concentration guidelines for water quality control in cooling towers.

The report summarizes interaction of ions in solution—especially those that can cause significant damage to a cooling system. Complex ion interactions can significantly increase the solubility of sparingly soluble salts in water. Parameters that effect solubility, such as ionic

strength, activity coefficients, ion associations, weak acid dissociation, and temperature are discussed in detail.

When predicting the behavior of ions in water, ionic-strength analyses, ion-association analyses and saturation analyses are performed for each cation and anion. This report discusses how software is designed to rigorously evaluate water chemistry through an ion-by-ion analysis) in cooling systems—a trial-and-error solution involving the simultaneous evaluation of a significant number of linear and non-linear relationships.

A number of specialty chemicals are used to control scale and corrosion in power plant cooling systems. This report includes two areas of use: (1) scale control via the use of threshold scale inhibitors and dispersants, and (2) corrosion inhibition for mild steel and copper alloys.

Source water chemistry provides the base information required to evaluate cooling water chemistry: the information provided in most water analyses must be converted to functional concentration units, weak acids require speciation, and the cation and anions must be balanced before the water chemistry can be evaluated for cooling water use. The report outlines procedures to review, modify, and prepare source water chemistry for analysis.

Generalized indices and water quality criteria are typically used to screen and evaluate potential water sources for cooling. Often these criteria are overly conservative, and consequently, many candidate water sources are considered unusable. This report develops a step-by-step procedure to analyze source water chemistry on a more realistic basis. Tools such as pH/speciation relationships, ion association, adjusted solubility constants, and others are provided to analyze the usability of degraded water and potable water for cooling systems.

This project developed a water quality calculator that can be used to conduct site-specific evaluations of source waters being considered for cooling water at power plants. The calculator incorporates the methodologies developed for speciating and balancing source water chemistry and utilizes analytical tools such as pH/speciation relationships, ion association, adjusted solubility constants, and others to evaluate source candidates quickly. Also, the calculator enables the user to easily assess the effects of cooling system pH and operating temperature. The calculator is provided online as an Excel spreadsheet (see Section 8).

Lastly, the intent of this report is to develop a methodology to evaluate source waters that could be used for power plant cooling systems. Considerations such as source water pretreatment, cooling system materials of construction, and zero liquid discharge strategies are not discussed.

## **Recommendations**

The water quality calculator and site-specific evaluation methodologies developed from this work should be used to determine the usability of degraded water sources for power plant cooling towers.

## **Benefits to California**

More than ever, increasing competition for potable water in California is reducing supplies and increasing costs. The water quality calculator and site-specific evaluation methodologies developed in this study enable power plant managers to much better evaluate the feasibility of using degraded water supplies for power plant cooling towers. As a result, these sources can

replace a portion of potable water supplies, which can be freed for other uses. California can benefit from a greater supply of potable water, and the ability of electricity generating companies to site power plants using cooling towers in areas that would otherwise not have a viable water source to supply those systems.

## 1.0 Introduction

There is a significant amount of pressure to utilize degraded water sources (non-potable water) for cooling for new power plants and repowering projects. Degraded water, by its very nature, is more difficult to use, because it usually contains constituents of concern that create problems in cooling systems. Many viable degraded water sources are eliminated from consideration, because the standard evaluation approach is overly simplistic and conservative. Water quality criteria for industrial cooling towers in the form of simple indices and general guidelines have been in use for a number of years. Many waters deemed unusable by the standard criteria are usable when evaluated with more sophisticated analytical tools. This project developed a methodology that allows the user to establish site-specific water quality criteria.

This report will cover the following related areas:

- The evolution of simple indices and the use of generalized guidelines for water quality criteria for cooling towers
- The chemistry of ion interaction and a more technical approach to developing water quality criteria
- Commercial software, and how it works
- The use of specialty chemicals to extend solubility criteria
- Source water data preparation
- Developing site specific water quality criteria for cooling towers

This project's intent was to develop a methodology to evaluate source waters that could be used for power plant cooling systems. Considerations such as source water pretreatment, cooling system materials of construction, and zero liquid discharge strategies are not discussed.

A water quality calculator, provided as an Excel spreadsheet, utilizes the site-specific evaluation methodologies developed in this project.

### 1.1. Report Organization

**Section 2, Indices and Guidelines.** Predicting the solubility of sparingly soluble salts<sup>1</sup> (such as calcium carbonate) in water has been a concern of municipal, commercial, and industrial system operators for many years. In the early 1900s, research into the effects of ion interaction of scaling salts was just being quantified and studied. Later, indices were developed to predict the behavior of calcium carbonate to protect water distribution systems from scale and corrosion. Water quality standards have since evolved for cooling systems that incorporate indices and concentration guidelines for scaling constituents such as calcium carbonate, calcium sulfate, silica, and others. This section discusses simple calcium carbonate prediction indices and concentration guidelines currently used to control water quality in cooling towers.

**Section 3, Ion Chemistry.** This section discusses the interaction of ions in solution, especially those that can cause significant damage to a cooling system. Complex ion interactions can

---

<sup>1</sup> *Sparingly soluble salts* have low solubilities.

increase the solubility of sparingly soluble salts in water. It also discusses parameters that effect solubility, such as ionic strength, activity coefficients, ion associations, weak acid dissociation, and temperature.

**Section 4, Software.** When predicting the behavior of ions in water, ionic-strength analyses, ion-association analyses and saturation analyses are performed for each cation and anion. This section discusses how software is designed to rigorously evaluate water chemistry (ion-by-ion analysis) in cooling systems—a trial-and-error solution involving the simultaneous evaluation of a significant number of linear and non-linear relationships.

**Section 5, Specialty Chemicals.** In addition to the customary bulk industrial chemicals used in cooling systems—such as sulfuric acid for pH control and sodium hypochlorite for microbiological control—a number of specialty chemicals are used to control scale and corrosion in power plant cooling systems. This section covers two areas of specialty chemical use: (1) scale control via the use of threshold scale inhibitors and dispersants, and (2) corrosion inhibition for mild steel and copper alloys.

**Section 6, Source Water Chemistry.** Source water chemistry provides the base information required to evaluate cooling water chemistry. The information provided in most water analyses must be converted to functional concentration units, weak acids require speciation, and the cation and anions must be balanced before the water chemistry can be evaluated for cooling water use. This section outlines procedures to review, modify, and prepare source water chemistry for analysis.

**Section 7, Site-Specific Analysis.** Generalized indices and water quality criteria are typically used to screen and evaluate potential water sources for cooling. Often these criteria are overly conservative, and consequently, many candidate water sources are considered unusable. This section incorporates theory from the previous chapters and develops a step-by-step procedure to analyze source water chemistry on a more realistic basis. Tools such as pH/speciation relationships, ion association, and adjusted solubility constants are provided to analyze the usability of water for cooling systems.

**Section 8, [Water Quality Calculator](#).** This project developed a water quality calculator to conduct site-specific evaluations of source waters being considered for cooling water at power plants. The calculator incorporates the methodologies developed for speciating and balancing source water chemistry and utilizes analytical tools such as pH/speciation relationships, ion association, adjusted solubility constants, and others to quickly evaluate source candidates. Also, the calculator enables the user to easily assess the effects of cooling system pH and operating temperature. It is provided as an Excel spreadsheet.

## **2.0 Indices and Guidelines**

### **2.1. Introduction**

Predicting the solubility of sparingly soluble salts (such as calcium carbonate) in water has been a concern of municipal, commercial, and industrial system operators for many years. In the early 1900s, research into the effects of ion interaction of scaling salts was just being quantified and studied. Later, indices were developed to predict the behavior of calcium carbonate (as well as calcium phosphate), to protect water distribution systems from scale and corrosion. More recently, cooling system water quality standards have evolved that incorporate indices and concentration guidelines for scaling constituents such as calcium carbonate, calcium sulfate, and silica. With the advent of desktop computing, commercially available models have been developed to predict the behavior of a variety of sparingly soluble salts. This section discusses simple calcium carbonate prediction indices and concentration guidelines currently used to control water quality in cooling towers.

### **2.2. Simple Indices**

In 1936, W. G. Langelier, an associate professor at the University of California at Berkeley, published a paper in the *Journal of the American Water Works Association* entitled “The Analytical Control of Anti-Corrosion Water Treatment.” This paper provided the scientific basis for what is commonly known today as the Langelier Saturation Index (LSI) (Langelier 1936). His work consisted of validating known chemical relationships involving calcium carbonate solubility and alkalinity/pH relationships with laboratory testing. The LSI, although limited in scope today, is still widely used by municipal, commercial, and industrial water users. A number of indices have followed, and the most common are the Ryznar Stability Index (RSI) and the Practical Scaling Index (PSI).

#### **2.2.1. Langelier Saturation Index**

Early in the 1900s, there was a pressing need to develop methods of predicting and controlling the tendency of water to corrode iron pipe in freshwater distribution systems such as those being installed by rapidly growing municipalities. Low doses of lime or soda ash were sometimes added to the water supply to raise pH or increase alkalinity to promote “controlled” calcium carbonate formation. At that time, it was generally accepted that a thin film of calcium carbonate provided a corrosion barrier between naturally oxygenated water and the wetted surfaces of iron pipe. Langelier developed his method to predict the pH at which calcium carbonate would be at saturation. This prediction method enabled municipal water suppliers to calculate the saturation pH of their water, adjust the pH as necessary, and minimize corrosion of their distribution piping.

The LSI is based on the relationship of calcium carbonate ( $\text{CaCO}_3$ ) pH, calcium concentration, total alkalinity concentration (also known as methyl orange, M alkalinity<sup>2</sup>), temperature, and background salt concentration (or Total Dissolved Solids, TDS). The original LSI relationships follow:

---

<sup>2</sup> Methyl orange is a titrating agent used to determine alkalinity.



$$pH_s = (pK_2 - pK_{SP, CaCO_3}) + pCa + pAlk \quad (1)$$

$$LSI = pH - pH_s \quad (2)$$

Where:	$pH_s$	pH at which $CaCO_3$ is at saturation
	$pK_2$	second dissociation constant for carbonic acid ( $HCO_3^{-1}$ to $CO_3^{-2}$ )
	$pK_{SP, CaCO_3}$	solubility constant for calcium carbonate
	$pCa$	minus of the logarithm of the molal concentration of $Ca^{+2}$ , $-\log(Ca^{+2}, \text{ moles}/1,000 \text{ grams water})$
	$pAlk$	minus of the logarithm of the molal concentration of M Alkalinity, $-\log(M \text{ Alkalinity}, \text{ moles}/1,000 \text{ grams water})$
	$pH$	measured pH of the solution
	molal	gram-moles of ion per 1,000 grams of water
	M Alkalinity	molal concentration of $HCO_3^{-1} + CO_3^{-2} + OH^{-1}$

Note that “molal” concentration is defined as moles of constituent per 1,000 grams of water. For example, a 0.1 molal concentration of  $Ca^{+2}$  is 0.1 moles of  $Ca^{+2}$  per 1,000 grams of water. The molecular weight of calcium is 40 grams, therefore a 0.1 molal concentration of  $Ca^{+2}$  is 4 grams per 1,000 grams of water. Molal concentrations are sometimes used in chemistry because water expands and contracts slightly depending on temperature. Using 1,000 grams of water (1 liter of water at standard conditions of 1 atmosphere and 20°C), uncertainty as a result of temperature is eliminated.

Equation 1 is the simplified version of Langelier’s derivation. At  $pH < 7$  and  $pH > 10.3$ , the original equation includes an additional calculation to account for measurable levels of acidity and basicity, which effect  $pH_s$ .

When the measured pH of the water is greater than  $pH_s$ , calcium carbonate will likely form (refer to Equation 2). Conversely, when pH is less than  $pH_s$ , calcium carbonate will not form (actually, existing calcium carbonate will slowly dissolve).

Langelier adjusted the values of  $pK_{SP, CaCO_3}$  and  $pK_2$  using temperature and TDS. As temperature increases, the solubility of calcium carbonate decreases. Also, as TDS increases (an approximation of ionic strength – discussed later in Section 3, Ion Chemistry), the values of  $pK_{SP, CaCO_3}$  and  $pK_2$  increase. The current version of the  $pH_s$  calculation (Equation 3) for LSI follows:

$$pH_s = 9.3 + A + B - C - D \quad (3)$$

Where:

$$A = 0.1 (\log (TDS, \text{mg/l}) - 1)$$

$$B = -13.12 \log (^{\circ}C + 273) + 34.55$$

$$C = \log (Ca^{+2}, \text{mg/l}_{CaCO_3}) - 0.4$$

$$D = \log (M \text{ alkalinity}, \text{mg/l}_{CaCO_3})$$

Note that the above relationships use concentration units common to water treatment, mg/l and mg/l<sub>CaCO<sub>3</sub></sub>. These units correspond to constituent concentrations expressed as milligrams per liter or milligrams of calcium carbonate equivalents per liter of water, respectively (calcium carbonate equivalency is discussed in detail in Section 6, Source Water Chemistry).

An LSI value greater than 0 identifies a scaling tendency; whereas, a value of less than 0 identifies a corrosion tendency (scale dissolving). In systems with carbon steel wetted surfaces, an LSI value of 0 to 1 (or more) is usually maintained in the presence of a polyphosphate and/or a scale inhibitor and/or a dispersant (discussed in Section 5, Specialty Chemicals).

It should be noted that the LSI only identifies the tendency of any given water to form calcium carbonate scale. Over time, the usefulness of the LSI as a basic prediction and control tool has diminished with a better understanding of factors that contribute to or inhibit scale formation, such as:

- pH at the surface of wetted metal surfaces can be higher than bulk water pH.
- Ion-to-ion interactions can “tie up” a significant amount of calcium with other ions (ion association is discussed in Section 3, Ion Chemistry).
- Scale inhibitors can significantly increase the degree of calcium carbonate saturation (by several orders of magnitude—corresponding to an LSI of 2).
- High flow/turbulent areas can tolerate slightly higher LSI values, e.g., condenser tubes.

Even though it has limitations, LSI (as well as RSI and PSI) has been integrated into most modern control strategies, because it is quick and easy to measure.

### 2.2.2. Ryznar Stability Index

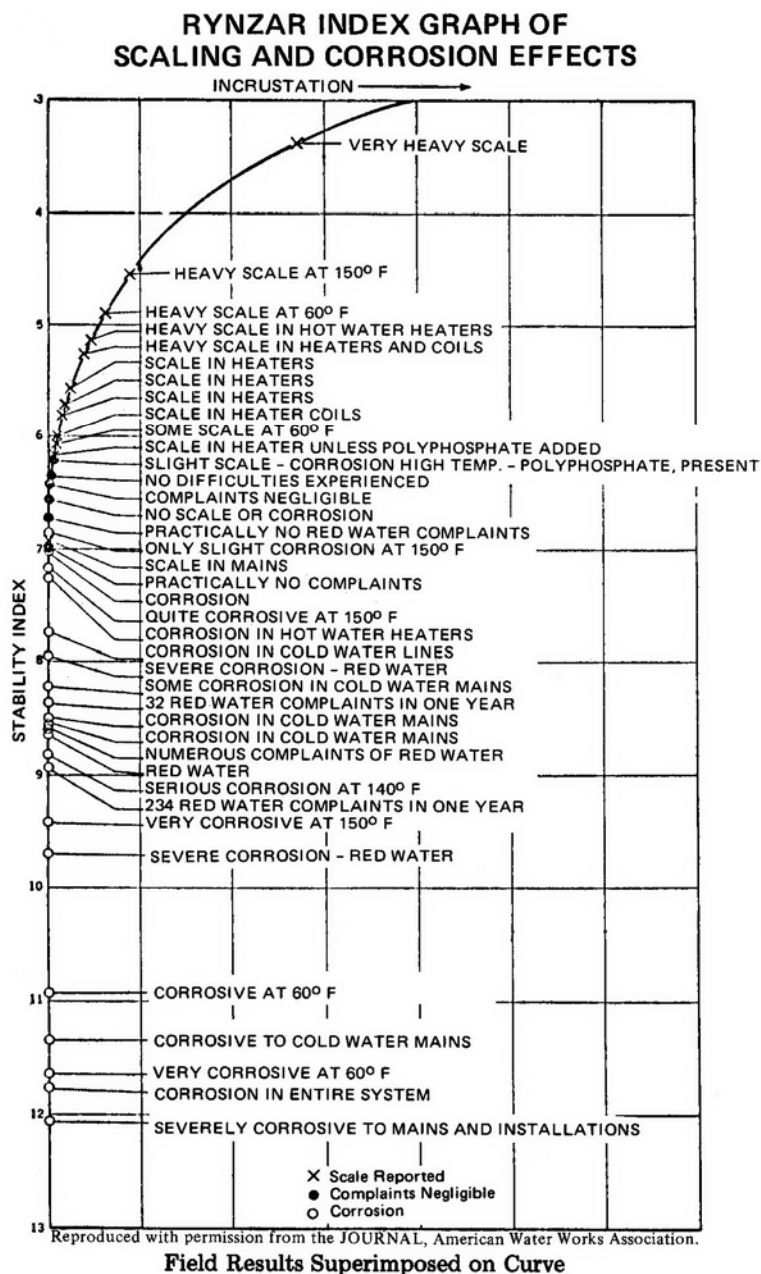
The Ryznar Stability Index (RSI) (Ryznar 1944) was an attempt to quantify the degree of scale formation and corrosion using LSI calculation elements:  $pK_{SP, CaCO_3}$ ,  $pK_2$ ,  $pCa$ ,  $pAlk$ , and  $pH_S$  (Equation 1). The Ryznar Stability Index calculation follows:

$$RSI = 2 pH_S - pH \tag{4}$$

Equation 3 can be used to calculate  $pH_S$ . The RSI was developed empirically by observing numerous water sources (in the Great Lakes area) and applications and their resultant scale and corrosion conditions. Refer to Figure 2-1 for a depiction of the Ryznar Stability Index.

The RSI not only identifies the tendency to scale or corrode, it also attaches a degree of severity. An RSI value greater than 6.0 identifies a corrosion (scale-dissolving) tendency, while a value of less than 6.0 identifies a scaling tendency. For example, a RSI value of 4.5 predicts “heavy scale at 150°F”; whereas a value of 9.4 predicts “very corrosive conditions at 150°F.” Refer again

to Figure 2-1. The same conditions and technological advances in scale inhibition that minimize the usefulness of the LSI also apply to the RSI.



(Graphic courtesy of U.S. Filter Corporation. *Water and Wastewater Treatment Handbook*, 19<sup>th</sup> printing, 1996.)

**Figure 2-1. Rynzar Stability Index Graph**

### 2.2.3. Practical Scaling Index

The PSI was an improvement over the LSI and RSI, because it relates cooling tower alkalinity to a calculated equilibrium pH (expressed as  $pH_{eq}$ ) (Puckorius and Loretitsch 1999). In cooling tower applications, alkalinity, which is in equilibrium with the atmosphere, can be relatively low, compared to the calcium concentration. Therefore, any interaction between calcium ( $Ca^{+2}$ ) and carbonate ( $CO_3^{-2}$ ) ions could reduce overall alkalinity in a cooling tower. Under these conditions pH would actually drop in the cooling tower as the relative concentration of  $CO_2$  increased ( $CO_2$  is in equilibrium with the air stream passing through the cooling tower)—thus eliminating the driving force to produce calcium carbonate scale. Cooling water  $pH_{eq}$  and the Practical Scaling Index are calculated as follows (Equations 5 and 6):

$$pH_{eq} = 1.465 \log(M \text{ Alkalinity, mg/l}_{CaCO_3}) + 4.54 \quad (5)$$

$$PSI = 2 pH_s - pH_{eq} \quad (6)$$

The equation for  $pH_{eq}$  (5), which is a function of alkalinity in a cooling tower, was developed empirically by reviewing actual operating data from numerous cooling towers (discussed in more detail in Section 6, Source Water Chemistry and Section 7, Site-Specific Analysis). Like the RSI, a PSI value greater than 6.0 identifies a corrosion (scale dissolving) tendency; whereas a value of less than 6.0 identifies a scaling tendency.

### 2.2.4. Concentration Guidelines

In addition to the indices discussed above, many simple control parameters have been developed for cooling systems and are also in general use today (e.g., the calcium sulfate solubility product, magnesium-silica solubility product, silica solubility limit). EPRI published water quality standards for electric utility cooling towers in 1982 (Micheletti et al. 1982) and revised their guidelines in 1998 (this document was not published) (Selby 1998). Refer to Table 2-1 for a summary of recent EPRI guidelines. This table is a compendium of a variety of sources and was extracted from a report jointly prepared by EPRI and the California Energy Commission. (DiFilippo 2002) The guidelines are very conservative, especially with the advent and acceptance of computer-based prediction tools and the development of more sophisticated chemical treatment approaches. (Threshold scale inhibitors, polymer dispersants, crystal modifiers, and others are discussed in Section 5, Specialty Chemicals).

Many of the guidelines are based on solubility relationships of pure salts in water (e.g., calcium sulfate, silicon dioxide ( $SiO_2$ ), and magnesium silicate). Generally speaking, these parameters should be used as a starting point in any analysis to determine operating parameters based on system temperature, pH, salt background, ion associations, treatment chemicals (scale inhibitors/dispersants), and others.

There are a number of power plants in the United States that have pioneered the use of treated municipal effluent for cooling tower make-up in the past 30 years. However, there was little guidance in the early standards to minimize calcium phosphate deposition (phosphate is a major constituent in treated municipal effluent). Typically the approach was to either remove the phosphate via precipitation softening or operate the cooling system at low pH (6.5 to 7.0) and low cycles of concentration (3 to 5). Significant progress has been made in the past ten

years with calcium phosphate control, with the development of many specialty chemicals that allow for a higher operating pH (to minimize corrosion potential) and higher cycles of concentration. Also, the more frequent use of treated effluent for cooling tower make-up as a means of conserving fresh water has helped to accelerate the development of these chemicals.

**Table 2-1. Water Quality Parameters for Cooling Towers**

Parameter	Units	EPRI 1982		Selby 1988
Ca	mg/l <sub>CaCO3</sub>	900 (max)		(Note 6)
Ca x SO <sub>4</sub>	mg/l <sup>2</sup>	----		500,000 (5)
Mg x SiO <sub>2</sub>	mg/l <sub>CaCO3</sub> x mg/l <sub>SiO2</sub>	35,000 (2)	75,000 (3)	35,000 (5)
M Alkalinity (1)	mg/l <sub>CaCO3</sub>	30–50 (2)	200–250 (3)	(Note 6)
SO <sub>4</sub>	mg/l	----		(Note 6)
SiO <sub>2</sub>	mg/l	150		150 (5)
Ortho-PO <sub>4</sub>	mg/l	< 5	(Note 4)	(Note 6)
Fe (Total)	mg/l	----		< 0.5 (5)
Mn	mg/l	----		< 0.5
Cu	mg/l	----		< 0.1
Al	mg/l	----		< 1
S	mg/l	----		5
NH <sub>3</sub>	mg/l	----		< 2 (8)
pH	----	6.8–7.2 (2)	(Note 6)	(Note 6)
TDS	mg/l	70,000		----
TSS (7)	mg/l	----		< 100–< 300
BOD	mg/l	----		(Note 9)
COD	mg/l	----		(Note 9)
Langelier SI	----	----		< 0
Ryznar SI	----	----		> 6
Practical SI	----	----		> 6

**Notes**

1. M Alkalinity (methyl orange titrating agent) =  $\text{HCO}_3^{-1} + \text{CO}_3^{-2} + \text{CO}_2 + \text{OH}^{-1}$
2. Without scale inhibitor.
3. With scale inhibitor.
4. No recommendation given because of insufficient data.
5. This is a conservative value. Reference is made to EPRI's SEQUIL RS (predictive software) to determine case-specific limits.
6. No value established. Reference is made to EPRI's SEQUIL RS (predictive software) to determine case-specific limits.
7. < 100 mg/l TSS with standard (sometimes known as high-efficiency) film fill and < 300 mg/l TSS with open (sometimes known as non-fouling) film fill or splash fill.
8. Limit applies when copper bearing alloys are present in the cooling system. This limit does not apply to copper nickel alloys, 90-10 or 70-30.
9. No value established.

This report focuses on the evaluation of the solubility relationships of the most common cooling system scaling salts—namely calcium carbonate ( $\text{CaCO}_3$ ), calcium sulfate ( $\text{CaSO}_4$ ), dicalcium phosphate ( $\text{CaHPO}_4$ ), calcium bicarbonate ( $\text{Ca}_3(\text{PO}_4)_2$ ),  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$ , and silica ( $\text{SiO}_2$ ). These constituents usually occur at high levels and thus can create significant deposition problems. Constituents such as iron (Fe), manganese (Mn), copper (Cu), aluminum (Al), sulfide (S), ammonia ( $\text{NH}_3$ ), biological oxygen demand (BOD), and chemical oxygen demand (COD) should be monitored (as applicable) in cooling towers. Some source waters (particularly well water) contain high levels of iron and manganese. Depending on operating conditions, iron and manganese deposits can form on heat transfer surfaces. As with other forms of scales, these can be controlled with inhibitors (discussed in Section 5, Specialty Chemicals). If levels of iron and manganese are very high, they are sometimes removed from the source water prior to make-up to the cooling tower. Iron, copper, and aluminum can be generated as by-products of corrosion in the cooling system as a result of poor pH control or improper corrosion inhibition (control strategies are also discussed in Section 5). Certain degraded waters (e.g., treated municipal effluent and excess water from oil production) contain sulfides, ammonia, and relatively high levels of BOD/COD. Sulfides can create scale-forming compounds, or under certain circumstances, an odor nuisance. Ammonia, BOD, and COD can encourage biological growth in the cooling system and thus require additional or intensive halogenation. Ammonia is also a corrosion agent with copper bearing alloys (refer to Note 8 in Table 2-1). Although the behavior of these constituents is not covered in this report, they should be considered when evaluating cooling water sources. Lastly, the guidelines provided in Table 2-1 for Fe, Mn, Cu, Al, S, and  $\text{NH}_3$  are generally accepted for power plant cooling systems.

### 3.0 Ion Chemistry

#### 3.1. Introduction

Section 2 discussed simple solubility indices and cooling tower concentration guidelines were. This section discusses complex ion interactions, which can significantly effect the solubility of sparingly soluble salts in water. Parameters that effect solubility, such as ionic strength, activity coefficients, ion associations, weak acid dissociation, and temperature are discussed. These parameters will be used in Section 7, Site-Specific Analysis, to predict solubility and cycles of concentration in cooling systems.

#### 3.2. Ionic Strength and Activity Coefficients

Ionic strength is a measure of the charge density of electrolytes (the ions of dissolved salts) in water, and is calculated as follows (Stumm and Morgan 1970):

$$I = 0.5 \sum m_i Z_i^2 \quad (7)$$

Where:  $I$  Ionic strength  
 $m_i$  Molarity of specie  $i$ , gram-moles/liter  
 $Z_i$  Valence (charge) of specie  $i$

For a simple solution containing salts of sodium, calcium, magnesium, bicarbonate, carbonate, chloride, and sulfate, ionic strength would be calculated as follows:

$$I = 0.5 ([Na^{+1}] + 4[Ca^{+2}] + 4[Mg^{+2}] + [HCO_3^{-1}] + 4[CO_3^{-2}] + [Cl^{-1}] + 4[SO_4^{-2}]) \quad (8)$$

Where:  $[ion]$  Molarity of ion, gram-moles/liter

Note that “molar” concentration is defined as moles of constituent per liter of water. For example, a 0.1 molar concentration of  $Ca^{+2}$  is 0.1 moles of  $Ca^{+2}$  per liter of water. The molecular weight of calcium is 40 grams, therefore a 0.1 molar concentration of  $Ca^{+2}$  is 4 grams per liter of water.

Note, there are some constituents, such as silica ( $SiO_2$ ) and boron (B), which are typically not included in the ionic strength calculation. Silica and boron exist in solution as weak undissociated acids, respectively as silicic acid and boric acid. At typical operating cooling tower pHs, they exist predominantly in the form of non-ionic orthosilicic acid ( $H_4SiO_4$ ) and boric acid ( $H_3BO_3$ ), with a very small fraction in the ionic form as  $H_3SiO_4^{-1}$  and  $H_2BO_3^{-1}$ . Also, there will be a number of ion associations in solution (discussed in Section 3.3) that are not charged, e.g.,  $CaSO_4^0$ ,  $CaCO_3^0$ , and  $MgSO_4^0$ . Again, these constituents are not included in the ionic strength calculation, because ionic strength is a measure of charge density.  $CaSO_4^0$ ,  $CaCO_3^0$  and  $MgSO_4^0$  are stable ion pairs that exist freely in solution in equilibrium with free ions and precipitating salts.

As the total dissolved solids (TDS) of a solution increases, charge density increases and electrostatic forces among and between ions in solutions interfere with ion interaction, thereby reducing “ion activity.” The net result is an apparent decrease in ion concentration. At infinite dilution, as ionic strength approaches zero, ion activity approaches ion concentration ( $\gamma_i=1$ ). The measure of ion activity is the activity coefficient, and is defined as follows:

$$A_i = \gamma_i m_i \quad (9)$$

Where:

$A_i$	Activity of specie $i$ (apparent concentration of specie $i$ )
$\gamma_i$	Activity coefficient of specie $i$ (a function of ionic strength)
$m_i$	Molarity of specie $i$ , gram-moles/liter

When evaluating ion association and solubility relationships, the activity coefficient is determined for each charged specie. A number of approximations for the activity coefficient have been developed over time—each for solutions with higher ionic strength. Refer to Table 3-1 for activity coefficient approximations. (Stumm and Morgan 1970; Ballard and Matson 1992). Early relationships were developed for solutions with relatively low ionic strength. For example, the initial estimating tool for the activity coefficient was developed by Debye and Hückel and it had an ionic-strength approximation limit of 0.005 which is equivalent to a 290 mg/l solution of sodium chloride. The limitation has increased over the years and the most recent approximation developed by Davies has an ionic-strength limit of 0.5 (equivalent to 29,000 mg/l solution of NaCl). Note that the other methods are usually in agreement (to the extent of their concentration limits) with the Davies approximation.

TDS is a measure of the dissolved salts in water, which includes ionic, non-ionic and associated forms, and is usually expressed as milligrams of dissolved salts per liter (mg/l) of solution. Ionic strength is a measure of ions in solution and is expressed as molarity (grams-moles per liter). An analysis was conducted for a simple salt solution (consisting of sodium, calcium, magnesium, bicarbonate, chloride and sulfate) to develop a simplified relationship for  $TDS_{Ion}$  to ionic strength. Figure 3-1 represents over 8,000 combinations of this hypothetical salt solution ranging from a  $TDS_{Ion}$  of 30 mg/l to 33,000 mg/l. A finite envelope defines the ionic strength –  $TDS_{Ion}$  relationship.  $TDS_{Ion}$  is the sum of the ions expressed as mg/l, e.g.,  $Na^{+1}$ ,  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $HCO_3^{-1}$ ,  $Cl^{-1}$ , etc. Note the significant spread to the data at higher  $TDS_{Ion}$  values.

The Ionic Strength –  $TDS_{Ion}$  relationship was then extended to calculating the Davies activity coefficient approximation found in Table 3-1. Refer to Figure 3-2. Activity coefficients for ion with a valence (charge) of  $\pm 1$ ,  $\pm 2$  and  $\pm 3$  were calculated and provided a fairly smooth/fairly narrow relationship to  $TDS_{Ion}$ . The data spread in the Ion Strength –  $TDS_{Ion}$  analysis was essentially eliminated by the Davies approximation. Note that the activity coefficients for the different valences are somewhat asymptotic at a  $TDS_{Ion}$  range of approximately 10,000 mg/l to 25,000 mg/l (ionic strength of 0.22 to 0.75). Also, depending on ion charge, activity can be significantly affected by ionic strength. The activity coefficient falls asymptotically to 0.73 for monovalent ions (valence of  $\pm 1$ ), 0.28 for divalent ions (valence of  $\pm 2$ ) and 0.06 for trivalent ions (valence of  $\pm 3$ ). The impact of this phenomenon is significant, e.g., at a  $TDS_{Ion}$  of 12,000 mg/l, the apparent concentration ( $A_i = \gamma_i m_i$ , Equation 9) of interactive trivalent ions, such as  $PO_4^{-3}$ , is



only 6% of the actual concentration of free  $\text{PO}_4^{3-}$ . The impact of this phenomenon is that the solubility of sparingly soluble salts is extended significantly when background  $\text{TDS}_{\text{Ion}}$  increases (e.g., when cycles of concentration are increased in a cooling tower). The simplified Activity Coefficient –  $\text{TDS}_{\text{Ion}}$  relationship will be used in Section 7 to develop site-specific water quality guidelines for cooling towers.

Lastly, to be conservative in the use of the data provided in Figure 3-2 (Activity Coefficients versus  $\text{TDS}_{\text{Ion}}$ ), the upper edge of the band of data for each valence should be used. This will provide a slightly higher value for the activity coefficient.

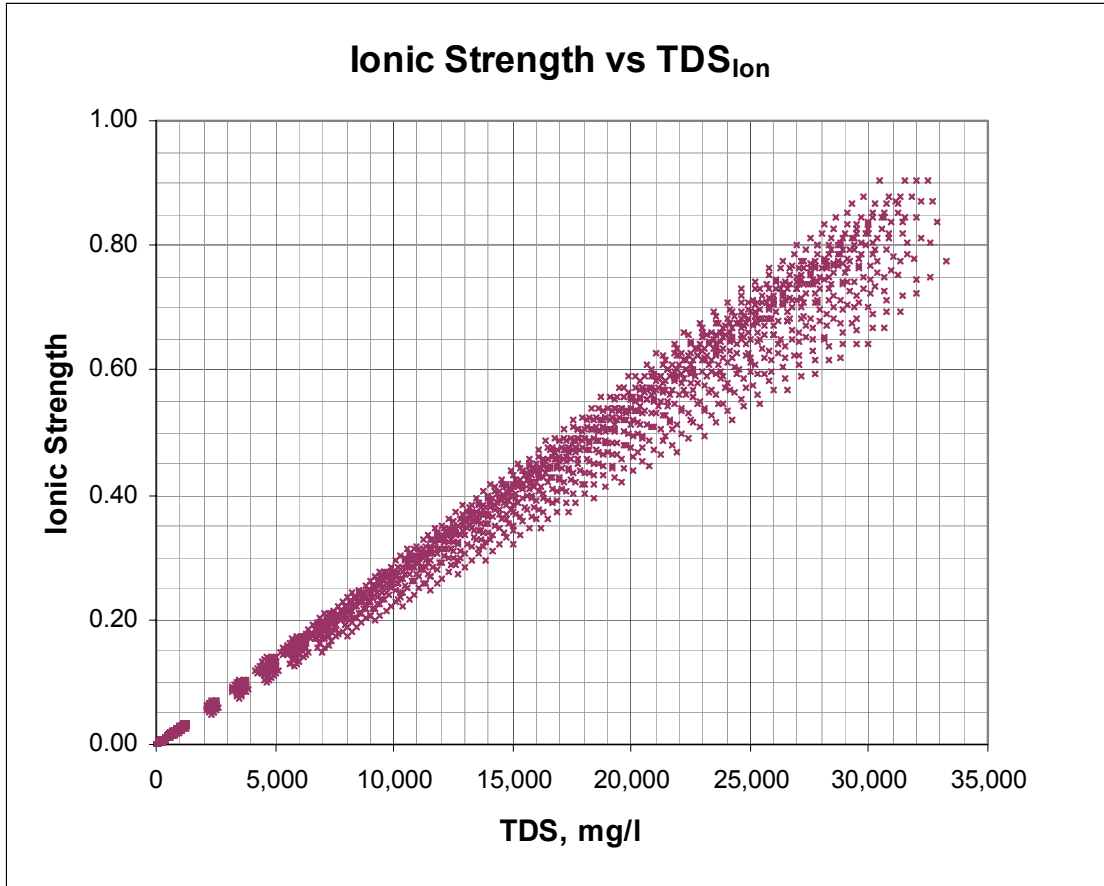
**Table 3-1. Activity Coefficient Calculation**

Approximation Method	Calculation	Applicability
Debye-Hückel (1)	$\log \gamma_i = -AZ_i^2 \sqrt{I}$	$I < 0.005$
Extended Debye-Hückel (2)	$\log \gamma_i = -AZ_i^2 \frac{\sqrt{I}}{1 + Ba\sqrt{I}}$	$I < 0.1$
Güntelberg	$\log \gamma_i = -AZ_i^2 \frac{\sqrt{I}}{1 + \sqrt{I}}$	$I < 0.1$ (3)
Davies	$\log \gamma_i = -AZ_i^2 \left\{ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right\}$	$I < 0.5$

**Notes**

- $\gamma_i$  = activity coefficient of specie  $i$ ,  $I$  = ionic strength,  $A \approx 0.51$  @  $25^\circ\text{C}$  (where  $A = 1.82 \times 10^6 (\epsilon T)^{2/3}$  and  $\epsilon$  is the dielectric constant for water,  $T$  is  $^\circ\text{K}$ ), and  $Z_i$  = charge of specie  $i$ .
- $B \approx 0.33$  @  $25^\circ\text{C}$  (where  $B = 50.3(\epsilon T)^{1/2}$  and  $\epsilon$  is the dielectric constant for water,  $T$  is  $^\circ\text{K}$ ), and “ $a$ ” is a parameter corresponding to ion size (angstrom units) as follows:

$a = 9$ for $\text{H}^{+1}$ , $\text{Al}^{+3}$ , $\text{Fe}^{+3}$	$a = 5$ for $\text{Ba}^{+2}$ , $\text{Sr}^{+2}$ , $\text{CO}_3^{-2}$
$a = 8$ for $\text{Mg}^{+2}$	$a = 4$ for $\text{Na}^{+1}$ , $\text{HCO}_3^{-1}$ , $\text{H}_2\text{PO}_4^{-1}$ , $\text{SO}_4^{-2}$ , $\text{HPO}_4^{-2}$ , $\text{PO}_4^{-3}$
$a = 6$ for $\text{Ca}^{+2}$ , $\text{Zn}^{+2}$ , $\text{Cu}^{+2}$ , $\text{Mn}^{+2}$ , $\text{Fe}^{+2}$	$a = 3$ for $\text{K}^{+1}$ , $\text{NH}_4^{+1}$ , $\text{OH}^{-1}$ , $\text{Cl}^{-1}$ , $\text{NO}_3^{-1}$ , $\text{HS}^{-1}$



**Figure 3-1.**

### 3.3. Ion Association

Ion association is a natural phenomenon that occurs in multi-component aqueous solutions of dissolved salts. Ions bond to form mono-molecular (ion-to-ion) associations that may or may not have a net charge. Refer to the following examples for sodium ( $\text{Na}^{+1}$ ), calcium ( $\text{Ca}^{+2}$ ), and magnesium ( $\text{Mg}^{+2}$ ) ion associations with common anions:

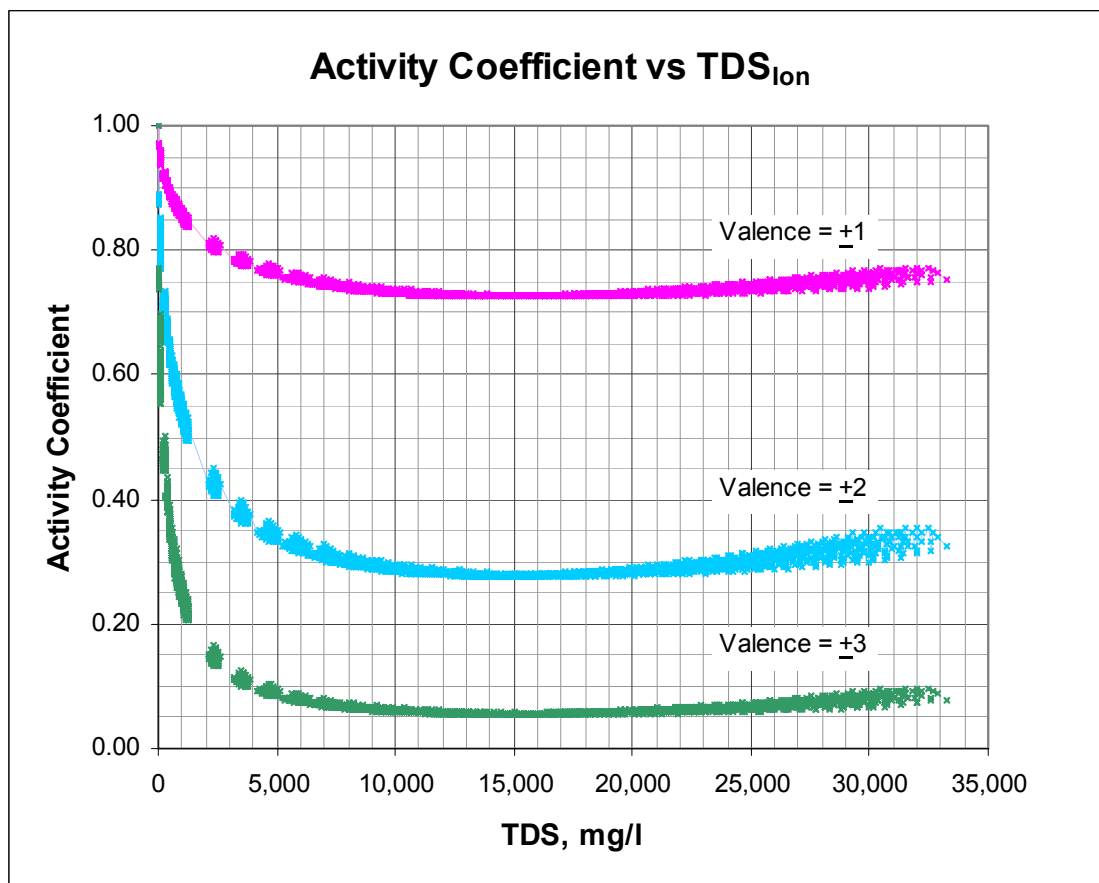
$$\begin{aligned}
 [\text{Na}_t] = & [\text{Na}^{+1}] + [\text{NaSO}_4^{-1}] + [\text{Na}_2\text{SO}_4^0] + [\text{NaHCO}_3^0] + [\text{NaCO}_3^{-1}] + \\
 & [\text{Na}_2\text{CO}_3^0] + [\text{NaCl}^0] + [\text{NaHPO}_4^{-1}]
 \end{aligned}
 \tag{10}$$

$$\begin{aligned}
 [\text{Ca}_t] = & [\text{Ca}^{+2}] + [\text{CaSO}_4^0] + [\text{CaHCO}_3^{+1}] + [\text{CaCO}_3^0] + [\text{CaOH}^{+1}] + \\
 & [\text{CaHPO}_4^0] + [\text{CaPO}_4^{-1}] + [\text{CaH}_2\text{PO}_4^{+1}]
 \end{aligned}
 \tag{11}$$

$$[Mg_i] = [Mg^{+2}] + [MgSO_4^0] + [MgHCO_3^{+1}] + [MgCO_3^0] + [MgOH^{+1}] + [MgHPO_4^0] + [MgPO_4^{-1}] + [MgH_2PO_4^{+1}] + [MgF^{+1}] \quad (12)$$

Where:  $[Na_i]$  Total molar concentration of soluble sodium, gram-moles/liter  
 $[Ca_i]$  Total molar concentration of soluble calcium, gram-moles/liter  
 $[Mg_i]$  Total molar concentration of soluble magnesium, gram-moles/liter

Therefore, Equations 10, 11, and 12 can be interpreted as the total molar concentration of sodium, calcium and magnesium in solution ( $Na_i$ ,  $Ca_i$ , and  $Mg_i$ ) and is equal to the free  $Na^{+1}$ ,  $Ca^{+2}$ , and  $Mg^{+2}$  plus ion-associated forms.



**Figure 3-2.**

Non-charged ion associations, such as  $CaSO_4^0$ , are not considered solid-phase precipitates, because they are typically “mono-molecular” in nature—ion pairs in solution. The “0” superscript for  $CaSO_4^0$  denotes a zero-valence (charge) ion pair. If the total concentration of  $Ca^{+2}$ ,  $SO_4^{-2}$  and the mono-molecular ion-pair of  $CaSO_4^0$  exceeds the saturation concentration of

CaSO<sub>4</sub> (e.g., a cooling tower operating at high cycles of concentrations), crystal-forming nuclei of CaSO<sub>4</sub> would start to form.

Ion concentrations typically reported in a general mineral analysis represent values for Na<sub>t</sub>, Ca<sub>t</sub>, Mg<sub>t</sub>, and others. Therefore, when sodium is reported to be at a concentration of 120 mg/l<sub>Na</sub>, this usually represents the total sodium in solution, Na<sub>t</sub>, which is equivalent to free sodium (Na<sup>+1</sup>) plus the sodium associated with the anions identified in Equation 10. Speciation analysis, which involves identifying specific ions or associations in solution (e.g., Ca<sup>+2</sup>, CaSO<sub>4</sub><sup>0</sup>, CaHCO<sub>3</sub><sup>+1</sup>, CaCO<sub>3</sub><sup>0</sup>, CaOH<sup>+1</sup>), is a very specialized area of analytical chemistry, and this type of data is not usually provided in standard water analyses. Some speciation analysis in the form of bicarbonate alkalinity (HCO<sub>3</sub><sup>-1</sup>), carbonate alkalinity (CO<sub>3</sub><sup>-2</sup>) alkalinity, non-ionized ammonia (NH<sub>3</sub>), and ionized ammonia (NH<sub>4</sub><sup>+1</sup>) is sometimes provided in standard water analyses. Variables such as pH, temperature, and exposure to atmospheric air will also affect the “speciation mix” of water.

Depending on the specific source of water, ions of concern can be significantly less than reported values (e.g., Ca<sup>+2</sup> and Mg<sup>+2</sup>). Therefore, simplistic methods that do not adjust concentrations for the common-ion effect are very conservative and typically understate solubility. There are some situations where calculated solubility is an order of magnitude higher (or more) by incorporating activity coefficient and common-ion evaluation methods.

Each ion association has an equilibrium relationship. As an example, the equilibrium relationship for calcium and sulfate in solution follows:



The mass-law relationship yields:

$$K_{fCaSO4} = \frac{\gamma_{Ca}[Ca^{+2}]\gamma_{SO4}[SO_4^{-2}]}{[CaSO_4^0]} \quad (14)$$

Restating Equation 14 using ion activity yields:

$$K_{fCaSO4} = \frac{A_{Ca}A_{SO4}}{[CaSO_4^0]} \quad (15)$$

Where:	$K_{fCaSO_4}$	$CaSO_4^0$ formation constant
	$[CaSO_4^0]$	$CaSO_4^0$ concentration, gram-moles/liter
	$A_{Ca}$	activity of the $Ca^{+2}$ ion, $A_{Ca} = \gamma_{Ca} \times [Ca^{+2}]$
	$A_{SO_4}$	activity of the $SO_4^{-2}$ ion, $A_{SO_4} = \gamma_{SO_4} \times [SO_4^{-2}]$

Rearranging Equation 15 yields:

$$[CaSO_4^0] = \frac{A_{Ca} A_{SO_4}}{K_{fCaSO_4}} \quad (16)$$

Note again, there is no activity coefficient for  $CaSO_4^0$  because it is not a charged ion. Other calcium relationships are similarly rearranged to yield:

$$[CaHCO_3^{+1}] = \frac{A_{Ca} A_{HCO_3}}{\gamma_{CaHCO_3} K_{fCaHCO_3}} \quad (17)$$

$$[CaCO_3^0] = \frac{A_{Ca} A_{CO_3}}{K_{fCaCO_3}} \quad (18)$$

$$[CaOH^{+1}] = \frac{A_{Ca} A_{OH}}{\gamma_{CaOH} K_{fCaOH}} \quad (19)$$

$$[CaHPO_4^0] = \frac{A_{Ca} A_{HPO_4}}{K_{fCaHPO_4}} \quad (20)$$

$$[CaPO_4^{-1}] = \frac{A_{Ca} A_{PO_4}}{\gamma_{CaPO_4} K_{fCaPO_4}} \quad (21)$$

$$[CaH_2PO_4^{+1}] = \frac{A_{Ca} A_{H_2PO_4}}{\gamma_{CaH_2PO_4} K_{fCaH_2PO_4}} \quad (22)$$

Combining Equations 17 through 22 to calculate total calcium ( $Ca_t$ ) yields:

$$[Ca_t] = [Ca^{+2}] + \frac{A_{Ca} A_{HCO_3}}{\gamma_{CaHCO_3} K_{fCaHCO_3}} + \frac{A_{Ca} A_{CO_3}}{K_{fCaCO_3}} + \frac{A_{Ca} A_{OH}}{\gamma_{CaOH} K_{fCaOH}} + \frac{A_{Ca} A_{HPO_4}}{K_{fCaHPO_4}} + \frac{A_{Ca} A_{PO_4}}{\gamma_{CaPO_4} K_{fCaPO_4}} + \frac{A_{Ca} A_{H_2PO_4}}{\gamma_{CaH_2PO_4} K_{fCaH_2PO_4}} \quad (23)$$

Rearranging Equation 23 to solve for free  $Ca^{+2}$  yields:

$$[Ca^{+2}] = [Ca_t] - \frac{A_{Ca} A_{HCO_3}}{\gamma_{CaHCO_3} K_{fCaHCO_3}} - \frac{A_{Ca} A_{CO_3}}{K_{fCaCO_3}} - \frac{A_{Ca} A_{OH}}{\gamma_{CaOH} K_{fCaOH}} - \frac{A_{Ca} A_{HPO_4}}{K_{fCaHPO_4}} - \frac{A_{Ca} A_{PO_4}}{\gamma_{CaPO_4} K_{fCaPO_4}} - \frac{A_{Ca} A_{H_2PO_4}}{\gamma_{CaH_2PO_4} K_{fCaH_2PO_4}} \quad (24)$$

When rigorously predicting the behavior of ions in water, ion-association analysis is done for each cation and anion. Refer to Table 3-2 for a summary of typical cation and anions included in this type of evaluation. Note that the table is not complete but is representative of the number of variables involved in this type of analysis. Similar types of ion association relationships (as shown in Equations 8, 9, and 10) exist for each cation and anion. Also, some ion pair concentrations are relatively significant, e.g.,  $CaSO_4^0$  and  $MgSO_4^0$  can comprise 20% to 30% of the total soluble  $Ca_t$  and  $Mg_t$  constituents. Most ion associations do not comprise a significant molar fraction of the total ion concentration, e.g.,  $CaCO_3^0$  could be 1% to 2% of the total calcium,  $Ca_t$ , while  $CaSO_4^0$  could be as high as 25% of the  $Ca_t$ .

**Table 3-2. Typical Cations and Anions Involved in Ion Association Analysis**

Cations	$Na^{+1}$ , $K^{+1}$ , $Ca^{+2}$ , $Mg^{+2}$ , $NH_4^{+1}$
Anions	$HCO_3^{-1}$ , $CO_3^{-2}$ , $Cl^{-1}$ , $SO_4^{-2}$ , $NO_3^{-1}$ , $NO_2^{-1}$ , $H_2PO_4^{-1}$ , $HPO_4^{-2}$ , $PO_4^{-3}$

Variables such as temperature, pH, and exposure to atmospheric air can significantly impact ion association relationships. Ion association formation constants and solubility constants are temperature dependent and must be evaluated at the hot/cold temperatures expected within a cooling system (including heat transfer surfaces). The pH affects the form of many anions (weak acids or bases). Refer to Figure 3-3 for variations in alkalinity, silica, phosphate, sulfide, boron, and ammonia species across a full pH range (0 to 14). In the pH range where cooling towers typically operate (6.5 to 8.5), some specie concentrations vary significantly, e.g.,  $H_2CO_3$ ,  $HCO_3^{-1}$ ,  $H_2PO_4^{-1}$ ,  $HPO_4^{-2}$  and  $H_2S$ ,  $HS^{-1}$ . These variations, in turn, affect ion association relationships. Exposure to air impacts  $CO_2$ ,  $H_2S$ , and  $NH_3$ —especially in cooling towers, which provide excellent air/water mixing. Because  $CO_2$ ,  $H_2S$ , and  $NH_3$  are dissolved gases, a fraction of each will volatilize into the air stream to maintain air/water equilibrium relationships. Also, as  $CO_2$  volatilizes to the air stream in the cooling tower, alkalinity equilibrium relationships strive to replace the stripped gas by shifting some of the bicarbonate alkalinity ( $HCO_3^{-1}$ ) to the

carbonic acid ( $\text{H}_2\text{CO}_3$  is an aqueous precursor to  $\text{CO}_2$ ).  $\text{H}_2\text{S}$  and  $\text{NH}_3$  will maintain equilibrium in the same manner.

Even though  $\text{PO}_4^{3-}$  levels appear to be negligible (or nonexistent) in Figure 3-4, cooling towers with phosphate in their make-up usually operate at pH levels less than 7.5 to minimize  $\text{Ca}_3(\text{PO}_4)_2$  scaling. At a pH of 7.5,  $\text{PO}_4^{3-}$  concentrations (as  $\text{PO}_4^{3-}$ ) may be as low as 1 to 5  $\mu\text{g/l}$  (micrograms per liter); however, because calcium phosphate is extremely insoluble, even this concentration level is a legitimate concern.

### 3.4. Saturation Concentrations of Precipitants

Non-associated ions are free to react in solution. Many associations exist as ion pairs of insoluble salts, e.g.,  $\text{CaSO}_4^0$  and  $\text{CaCO}_3^0$ , and as the concentration of ion pairs as well as free ions ( $\text{Ca}^{+2}$ ,  $\text{SO}_4^{-2}$  and  $\text{CO}_3^{-2}$ ) increase, they reach their solubility or saturation limit. When the solubility limit is exceeded, the solution is said to be supersaturated and precipitation will occur. At supersaturation, free ions start to nucleate into seed crystals and thus form precipitates or scale. Also, mono-molecular ion associations of supersaturated salts are attracted to the nucleation sites and are incorporated into the nucleation process. For example, the solubility relationship for calcium sulfate is defined as follows:

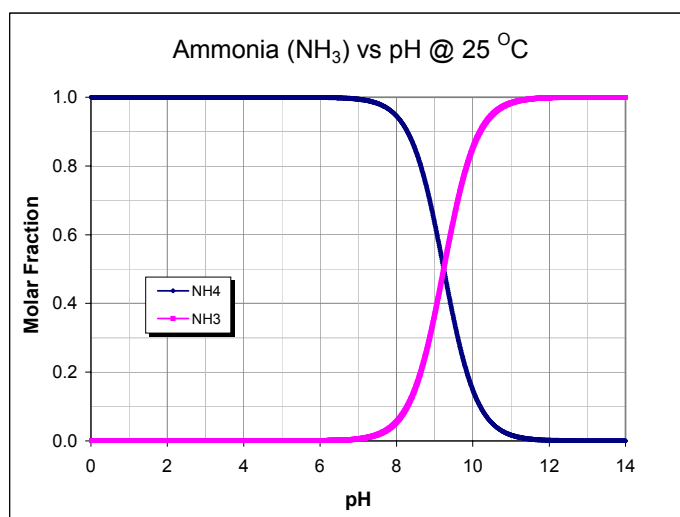
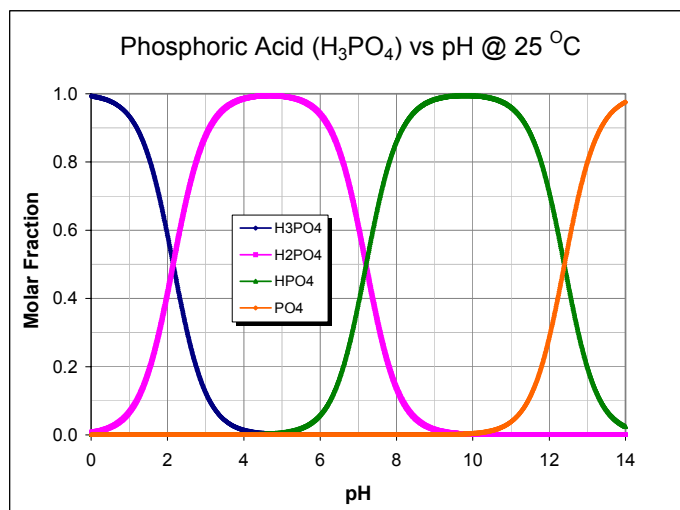
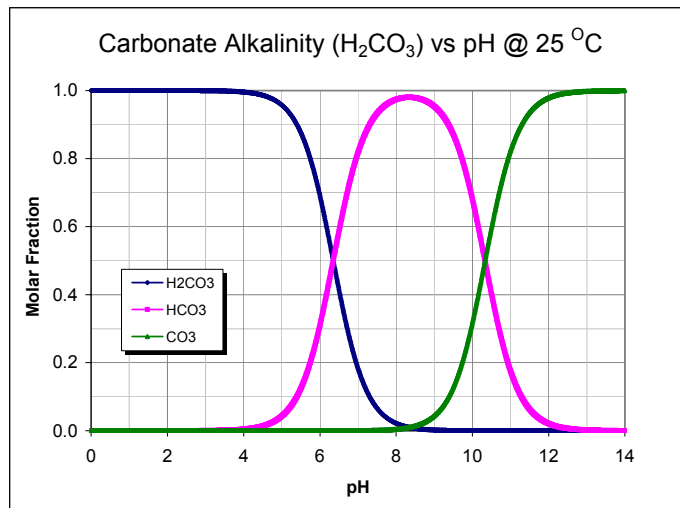
$$K_{SP, \text{CaSO}_4} = \gamma_{\text{Ca}} [\text{Ca}^{+2}] \gamma_{\text{SO}_4} [\text{SO}_4^{-2}] \quad (25)$$

Where:	$K_{sp, \text{CaSO}_4}$	Solubility product of calcium sulfate
	$[\text{Ca}^{+2}]$	Free $\text{Ca}^{+2}$ concentration, gram-moles/liter
	$[\text{SO}_4^{-2}]$	Free $\text{SO}_4^{-2}$ concentration, gram-moles/liter
	$\gamma_{\text{Ca}}$	Activity coefficient for $\text{Ca}^{+2}$
	$\gamma_{\text{SO}_4}$	Activity coefficient for $\text{SO}_4^{-2}$

When the product of  $\gamma_{\text{Ca}} \times [\text{Ca}^{+2}]$  and  $\gamma_{\text{SO}_4} \times [\text{SO}_4^{-2}]$  equals or exceeds  $K_{sp, \text{CaSO}_4}$ , calcium sulfate is said to be at saturation or supersaturation, respectively. The degree of saturation is known as saturation index (SI) and defined as:

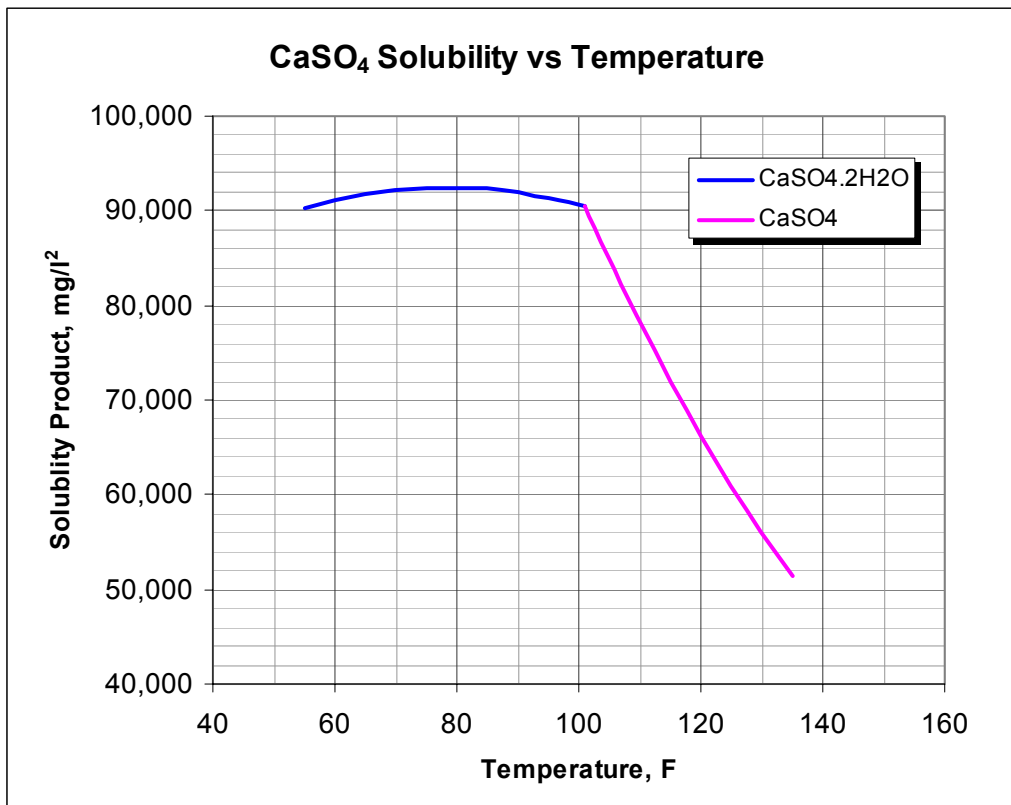
$$SI_{\text{CaSO}_4} = \frac{\gamma_{\text{Ca}} [\text{Ca}^{+2}] \gamma_{\text{SO}_4} [\text{SO}_4^{-2}]}{K_{SP, \text{CaSO}_4}} \quad (26)$$

For the above example, when  $SI_{\text{CaSO}_4} < 1$ , the solution is unsaturated with respect to calcium sulfate and nucleation will not occur. When  $SI_{\text{CaSO}_4} = 1$ , the solution has reached saturation. When  $SI_{\text{CaSO}_4} > 1$ , the solution is saturated and nucleation will initiate.



**Figure 3-3. Variations in alkalinity, silica, phosphate, sulfide, boron, and ammonia species**





**Figure 3-4. CaSO<sub>4</sub> solubility vs. temperature**

Lastly, solubility products are also a function of temperature. Refer to Figure 3-4 for an example of the solubility-temperature relationship for calcium sulfate. Calcium sulfate has a variety of precipitation products; however, at cooling system temperatures, the most likely forms will be gypsum (CaSO<sub>4</sub>•2H<sub>2</sub>O) and anhydrite (CaSO<sub>4</sub>). In Figure 3-4, gypsum will likely form when saturation conditions are at temperature less than 110°F/43°C. Note, gypsum solubility is proportional to temperature at less than 90°F/32°C to 95°F/35°C and inversely proportional at higher temperatures (less soluble). For a given concentration of calcium sulfate at different temperatures, the form and solubility of the salt will change, depending on cooling system location. In a cooling system, the temperature will cycle up to condenser outlet temperature (e.g., 115°F/46°C) and then drop to basin temperature (e.g., 75°F/24°C). Therefore, depending on the constituent salt of concern, cooling system location will dictate whether saturation is a concern and the type of the scale likely to form.

## **4.0 Software**

### **4.1. Introduction**

When predicting the behavior of ions in water, ionic-strength analyses, ion-association analyses, and saturation-index analyses are performed for each cation and anion. *Given the number of possible species and operating variables, a rigorous ion-by-ion analysis cannot be reasonably accomplished without a computer.* (Ferguson et al. 1994) The overall analysis embodies a trial-and-error solution involving the simultaneous evaluation of a significant number of linear and non-linear equations.

### **4.2. State of the Art**

A number of predictive software products have been developed in the past ten years (corresponding to the advent of desktop computing) to analyze water for a number of uses and impacts (e.g., cooling water, geothermal brine, oil-field produced water). The breadth of available products covers a broad range—from simple calculators to very sophisticated/comprehensive evaluation tools. Also, EPRI has developed software (SEQUIL RS) to predict cooling water behavior in cooling systems. This software product was developed through its first phase; follow-on phases using iterative analysis of key variables were never completed. Lastly, unless these software products are used frequently, the cost for this type of analysis can be very prohibitive.

### **4.3. General Calculation Approach**

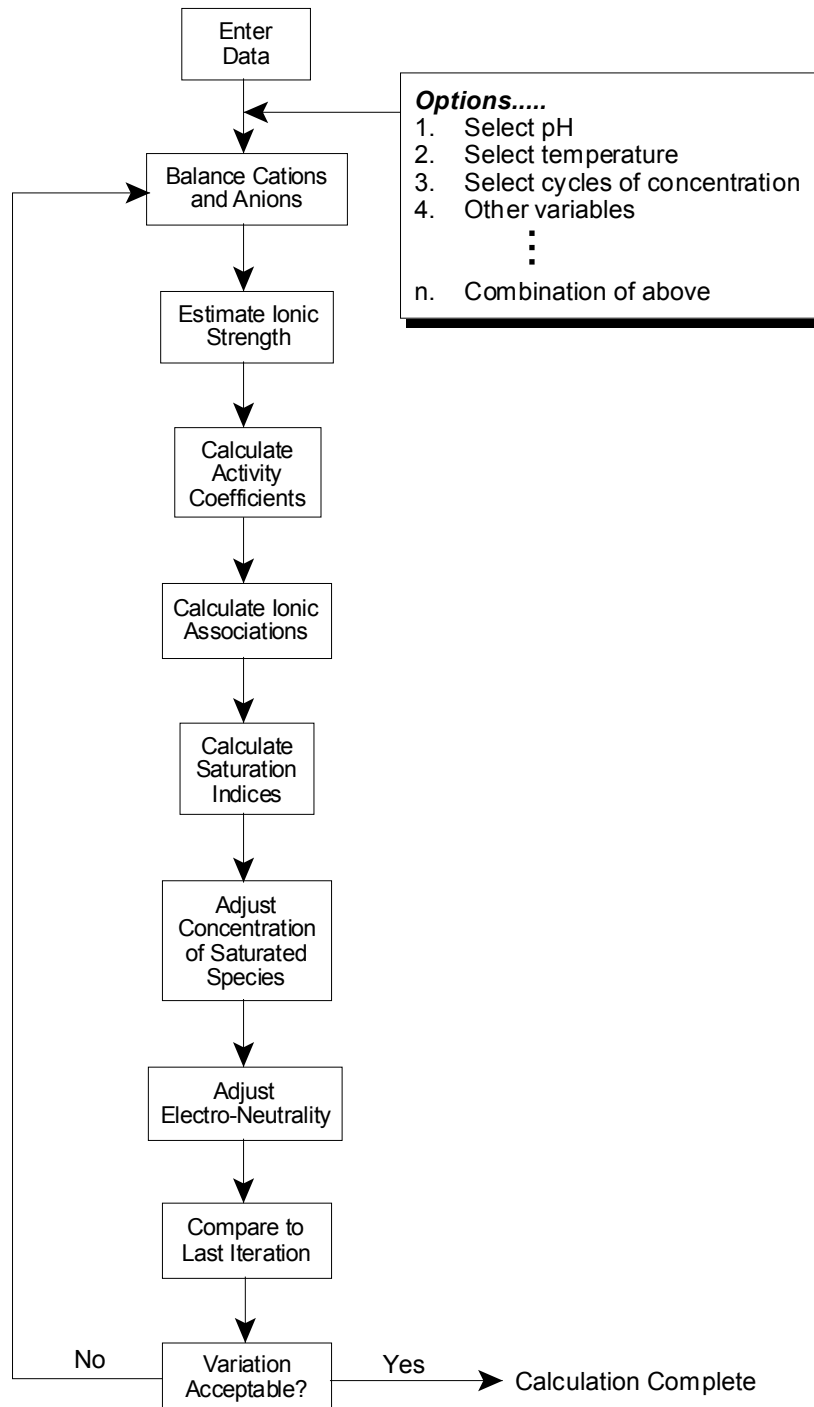
Generally, the following type of analysis occurs with software that is designed to evaluate complex solutions of electrolytes. Also, refer to Figure 4-1.

1. The water analysis must be checked for balance (i.e., the total cation equivalent concentration should equal the total anion equivalent concentration). Usually, sodium or chloride is adjusted to achieve equivalence. If the adjustment is more than 10% to 15% of total cation or anion equivalents, then the water analysis is likely flawed and another should be obtained.
2. Determine the calculation mode. Some typical calculation modes follow:
  - Select operating pH (automatically adjust total alkalinity), cycles of concentration, and temperature; and calculate resulting chemistry (identify saturation indices for applicable species).
  - Select operating pH (automatically adjust total alkalinity), cycles of concentration, and temperature; calculate resulting chemistry and adjust chemistry (downwards as required) for supersaturated species.
  - Select operating pH (automatically adjust total alkalinity) and temperature, and calculate maximum cycles of concentration and resulting chemistry.
3. Ionic strength is estimated assuming all ions are non-associated. The Davies approximation is usually employed because of its broad range (refer to Section 3, Ion Chemistry).

4. Using the ionic strength estimate, activity coefficients, molar fractions and ionic associations are calculated. Note that each calculation set must obey the electro-neutrality rule: charged cation equivalents must equal charged anion equivalents.
5. The saturation index for all precipitating species is then checked. If saturation is exceeded, the species affected by this analysis can be adjusted. Recheck results for electro-neutrality and adjust as required.
6. The calculation is reiterated (steps 2 through 5) until set-to-set changes are minimal.

A description of the water quality calculator is provided at the end of this report, in Section 8. The calculator performs basic (non-iterating) speciation, ionic strength, ion association, and saturation calculations for a limited number of constituents. The calculator mimics the software processes described in steps 1, 3, and 4 above.

## Generalized Calculation Procedure



**Figure 4-1.**

## **5.0 Specialty Chemicals**

### **5.1. Introduction**

In addition to the customary chemicals used in cooling systems, such as sulfuric acid for pH control and sodium hypochlorite for microbiological control, there are a number of specialty chemicals that are used to control scale and corrosion in power plant cooling systems. This section covers two areas of specialty chemical use: (1) scale control via the use of threshold scale inhibitors and dispersants, and (2) corrosion inhibition for mild steel and copper alloys.

### **5.2. Scale Control**

This section discusses two types of scale-control chemicals: (1) threshold inhibitors, and (2) dispersants. These represent the norm of control strategies used for cooling system scale control. When scale control is implemented via threshold inhibitors and dispersants, it is assumed that sparingly soluble salts are supersaturated (at concentrations in excess of the solubility) in the cooling system. Threshold inhibitors control the rate of crystal formation, distort crystal formation, and limit crystal growth; whereas, dispersants inhibit the deposition of scale via suspending crystal matter in solution. Both types of chemical control promote the formation of soft scale, which can be easily removed with mechanical cleaning. Conversely, if control chemicals are not utilized, tenacious scale incrustations can form. Also, controlling the rate of crystal growth and suspending precipitating matter allows the cooling system to expel most products of scale formation via blowdown before they have time to deposit and foul heat transfer surfaces. Low-flow regions, such as the cooling tower basin, are still vulnerable to accumulation and deposition of scale matter regardless of treatment.

Most, if not all power plants, utilize specialty chemicals for scale control, especially in the Southwest, where source water can have high levels of hardness, alkalinity, and sulfate. To avoid the use of specialty chemicals in water with a potential for scale formation, a cooling system would have to be operated at low cycles of concentration, and depending on source-water constituents such as alkalinity and calcium, the pH of the recirculating water may have to be maintained at a low level, creating corrosion concerns. Also, operation at low cycles of concentration is not feasible for many plants, especially inland plants in California that must operate in a zero-discharge mode. Lastly, plants utilizing degraded water, such as treated municipal effluent, must use specialty chemicals to control scale (e.g., calcium phosphate formation).

#### **5.2.1. Threshold Scale Inhibitors**

Phosphonates are used primarily as calcium carbonate and calcium phosphate ( $\text{CaCO}_3$  and  $\text{Ca}_3(\text{PO}_4)_2$ ) threshold-scale inhibitors in cooling tower systems, as well as for calcium sulfate ( $\text{CaSO}_4$ ) control in high-sulfate source waters. Threshold inhibitors do not prevent scale formation; instead they slow the growth rate of nucleating crystals. Nucleation occurs when a significant concentration of ion pairs and free ions (supersaturation) start to accumulate as crystal seeds. Nucleation can also occur on substrate materials such as airborne silt drawn into the cooling tower by the air stream. Recall, ion pairs are single molecules of a scaling salt, e.g., one calcium ion combined with one carbonate ion to form  $\text{CaCO}_3^0$ . Many commonly used threshold inhibitors contain phosphonic acid functional groups,  $-\text{PO}(\text{OH})_2$  (there are other types of threshold inhibitors such as carboxylic acid). These functional groups form complexes with multivalent cations (e.g.,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Fe}^{+2}$ ,  $\text{Al}^{+3}$ ) by releasing  $\text{Na}^{+1}$  or  $\text{H}^{+1}$  ions in exchange

for cations. Refer to Table 5-1 for a summary of three common phosphonate inhibitors, along with their chemical name and structure. The resulting phosphonate-metal complex becomes entrapped with nucleating ion pairs and is incorporated into the crystal growth process. These relatively large molecules interfere with orderly nucleation and crystal growth. Depending on pH, the concentration of multivalent cations and number of nucleating ion pairs, threshold inhibitors can obstruct crystal growth significantly enough to create bonding and surface stresses with the nucleating crystals that either slow or prevent further growth. Typically, crystal growth is slowed enough (and in some cases stopped) to permit accumulation to be controlled via blowdown. If significant crystal accumulation is expected, dispersants can be used to prevent crystals from falling out of solution and fouling heat transfer surfaces (discussed next in this section).

**Table 5-1. Common Phosphonate Threshold Inhibitors**

HEDP	1-Hydroxyethylene-1,1-diphosphonic acid	$  \begin{array}{c}  \text{O} \quad \text{OH} \quad \text{O} \\  \parallel \quad   \quad \parallel \\  \text{HO} \text{---} \text{P} \text{---} \text{C} \text{---} \text{P} \text{---} \text{OH} \\    \quad   \quad   \\  \text{HO} \quad \text{CH}_3 \quad \text{OH}  \end{array}  $
AMP	Aminomethylenephosphonic acid	$  \begin{array}{c}  \text{O} \\  \parallel \\  \text{HO} \text{---} \text{P} \text{---} \text{CH}_2 \text{---} \text{NH}_2 \\    \\  \text{HO}  \end{array}  $
PBTC	2-Phosphonobutane-1,2,4-tricarboxylic acid	$  \begin{array}{c}  \text{HO} \quad \text{OH} \\  \diagdown \quad / \\  \text{P}=\text{O} \\    \\  \text{CH}_2 \text{---} \text{C} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \\    \quad   \quad   \\  \text{COOH} \quad \text{COOH} \quad \text{COOH}  \end{array}  $

Threshold inhibition does not occur on a predictably stoichiometric basis (i.e., X mg/l of inhibitor required for Y mg/l of calcium). Because phosphonate inhibitors form complexes with hardness ions and interrupt crystal formation kinetics, one equivalent of PBTC can successfully control 100 to 3,000 equivalents of  $\text{CaCO}_3$  or  $\text{Ca}_3(\text{PO}_4)_2$ . (Vanderpool 1997) For example, as little as 5 to 10 mg/l of PBTC can inhibit calcium carbonate to 100 to 300 times saturation (LSI equivalent to 2.3 to 2.5). (Puckorius and Loretitsch 1999)

Oxidative agents used for microbial control can degrade phosphonate compounds, e.g., sodium hypochlorite ( $\text{NaOCl}$ ), sodium bromide ( $\text{NaBr}$  in conjunction with  $\text{NaOCl}$ ), ozone ( $\text{O}_3$ ), and chlorine dioxide ( $\text{ClO}_2$ ). If the oxidizing agent interacts (comes into chemical contact) with the threshold inhibitor, the phosphonate functional group is cleaved from the inhibitor molecule and oxidized to orthophosphate,  $\text{PO}_4^{3-}$  (or one of its other pH-dependent forms). Oxidation therefore renders the complexation function ineffective and generates a potential source of scale in the form of calcium phosphate. Calcium phosphate is very insoluble, especially at pH greater than 7.5. Cooling towers operating at high cycles of concentration, where threshold inhibitors

can remain in a cooling system for long periods of time (ten days or greater) (Hoots 1999 and Chmelovski 1996), are more susceptible to oxidative attack. In other words, the longer a phosphonate molecule is in a cooling system, the more likely it will interact with an oxidizing agent, particularly in systems that carry a halogen residual.

The following equation can be used to determine residence time for inhibitors in cooling systems:

$$t = -\ln \left[ \frac{C_i}{C_{i,t=0}} \right] \left[ \frac{V}{B+D} \right] \div 1440 \quad (27)$$

Where:	$t$	Residence time to reach a specific depletion concentration, days
	$C_i$	Depleted concentration of inhibitor $i$ at time $t$ , mg/l
	$C_{i,t=0}$	Concentration of inhibitor $i$ at time $t=0$ , mg/l
	$V$	Volume of the cooling system (not just the basin), gallons
	$B$	Blowdown rate, gpm
	$D$	Drift rate, gpm

Consider a 500-MW, combined-cycle plant operating at 20 cycles of concentration with the following cooling system characteristics:

$E$	3,500 gpm, evaporation rate
$N$	20 cycles of concentration
$Circ$	125,000 gpm, cooling system recirculation rate
$DF$	0.006%, drift fraction, percent of recirculation rate
$C_i$	5 mg/l, PBTC (assuming 75% depletion)
$C_{i,t=0}$	20 mg/l, PBTC
$V$	2,500,000 gallons
$B$	$E/(N-1) = 176.7$ gpm
$D$	$Circ \times DF = 7.5$ gpm

Solving for  $t$  using Equation 27 yields a residence time of 11.3 days for a given amount of PBTC to deplete 75% from 20 mg/l to 5 mg/l. It also assumes that fresh inhibitor is being added to compensate for losses as a result of blowdown. Inhibitor depletion is typically calculated on a 50% to 75% basis. Specialty chemical providers prefer a ten-day residence time limit for inhibitor depletion to avoid significant risk of oxidative attack. Note, regardless of the ten-day preference, some zero-discharge cooling systems must operate at high cycles of concentration,

and thus longer residence times. At high cycles of concentration, overfeeding of threshold inhibitors in excess of 25% to 35% may be required to compensate for losses created by oxidation of the phosphonate function of PBTC. Given the conditions in the above example, additional treatment in the form of dispersant control will be required to suspend  $\text{Ca}_3(\text{PO}_4)_2$  created by inhibitor decomposition byproducts (dispersants, which act to keep precipitating salts in suspension, will be discussed next in this section). One possible benefit of oxidation by-products could be enhanced corrosion protection via controlled deposition of  $\text{Ca}_3(\text{PO}_4)_2$  (this is highly dependent on variables such as cooling system calcium and pH).

Some manufacturers claim their phosphonate compounds are stable in the presence of oxidizers such as chlorine—so called “stabilized” compounds (Hoots 1999). Although this may be the case, it is prudent to develop a program with the assumption that there will be inhibitor loss from oxidation. If at a later date it is proven that the stabilized inhibitor formula is indeed stable in the presence of oxidizing biocides, the rate of feed— and thus the cost of treatment— can be reduced.

### **5.2.2. Polymer Dispersants**

Dispersants attract and attach to nucleating crystals in the bulk cooling water, interfere with the growth process, and prevent scale deposition by suspending crystals and other matter in solution. Polymer dispersants consist of chains or strands containing charged functional groups. Polymers that consist of a single type of functional group are designated mono-polymers (or just polymers), e.g., PAA (polyacrylic acid). Many polymers have fairly complex functional groups (e.g., the complexity of AMPS). Refer to Table 5-2 for examples of common mono-polymers. Polymers are often “mixed”, i.e. more than one type of functional group on a polymer chain, to form co-polymers (two different functional groups), ter-polymers (three groups), and quad-polymers (four groups). Quad polymers are a fairly recent innovation. For example, a PAA/sulfonated co-polymer would consist of “n” groups of acrylic acid functions and “r” groups of sulfonated functions. Again, refer to Table 5-2.

Functionality and the number and ratio of groups attached to a polymer strand are usually selected based on a specific application or need, e.g., calcium phosphate dispersion in high-hardness, high-pH cooling water. Also, the ratio of groups can be varied significantly, e.g., a ter-polymer could consist of a blend of three functional groups with a group mix ratio of 13:7:3 or 6:11:2 or 2:23:1. The possible combinations are only limited to the physical and chemical stability of formulations. Specialty chemical providers are constantly developing polymer blends to meet more difficult cooling water needs generated by cooling systems operating at higher cycles of concentration or using degraded or reclaimed water as make-up. Unfortunately, there is no method of predicting polymer performance based on the “design” of the molecule. Polymer blends are usually tested in laboratory simulations and in the field to verify efficacy.

Typically, dispersants are relatively short-chained, with a molecular weight of 2,000 to 4,000 daltons (one dalton is equivalent to a molecular weight of 1 gram per mole). For example, a PAA mono-polymer with a molecular weight of 3,000 daltons would consist of approximately 40 linked acrylic acid groups. Molecular weight is particularly important. Larger polymer strands (molecular weight greater than 10,000 daltons) act to flocculate crystals and effectively allow them to settle, which is contrary to the role of a dispersant.



Polymers in solution are highly charged, tangled strands containing functional sites. Refer to Figure 5-1 for a representation of dispersant polymer-crystal interaction. Functional groups form complexes (much in the same manner as phosphonates) with multivalent cations and embed into nucleating crystals. Thus, one or more nucleating crystal(s) is entangled in and around polymer strands. Once enmeshed with the polymer, the rate of crystal growth slows or completely stops. The overall anionic or negative charge of the polymers cause them to repel each other, and hence keep inhibited crystals (and other matter) in suspension forming soft-scale products and limiting deposition on heat transfer surfaces. Also, depending on the size of the crystal and the number and location of embedded strands, polymers can perform as crystal modifiers by creating bonding and internal/surface stresses. As a result, the “modified” crystal develops with rounded edges, as opposed to sharp planes, and has difficulty attaching to other crystals or surfaces (e.g., heat transfer surfaces).

Dispersants are added at levels of 5 to 50 mg/l (or more) depending on variables such as pH, temperature, flow conditions (at heat transfer surfaces), and calcium, magnesium, alkalinity, phosphate, and sulfate concentrations. Many times they are used in concert with phosphonate threshold inhibitors, especially in cooling systems where sparingly scale-forming salts are at exceedingly high saturation levels. Also, when cooling towers are operated at high cycles of concentration and the potential for phosphonate degradation is high (long retention time in the presence of oxidizing biocides), dispersants are used to suspend degraded phosphonate precipitation products such as calcium phosphate. Polymer dispersants have been successfully used to suspend calcium phosphate to 1,000 times saturation (recall, even at these levels of saturation, calcium phosphate crystal concentrations may only be 0.1 mg/l).

### **5.3. Corrosion Control**

Operating at lower pH ranges (6.5 to 7.5) to prevent calcium phosphate formation and deposition, iron and copper corrosion becomes a significant concern. There are a number of specialty chemicals used for corrosion control for mild steel and copper alloys. Iron will corrode readily in a cooling system rich in dissolved oxygen and in the presence of an electrically conductive salt solution (generally, the higher the TDS, the greater the need for corrosion protection). Corrosion inhibitors protect metal surfaces by physically establishing an insulating film over the surface of the metal, e.g., a polyphosphate/calcium carbonate film. Copper corrosion is prevented in much the same manner, with the use of a family of chemicals known as azoles that interact with the surface of copper alloys to form a tenacious film that blocks the formation of corrosion cells.

To accommodate poor make-up water quality, some new power plants are being built with a combination of corrosion-resistant titanium alloy heat transfer surfaces, fiberglass cooling tower structural components, non-metallic structural fasteners, and other features. Some power plant developers find it cost effective to invest in corrosion-resistant cooling system components to avoid the cost of maintenance and downtime resulting from corrosion-related problems.

**Table 5-2. Common Dispersants**

	Chemical Name	Functional Group
PAA	Polyacrylic acid	$\left[ \text{CH}_2 - \underset{\text{CHOOH}}{\text{CH}} \right]_n$
PMA	Polymaleic acid	$\left[ \underset{\text{CHOOH}}{\text{CH}} - \text{CH} \right]_p$
	Polycarboxylate ( $\text{Na}^{+1}$ salt, anhydrous form)	$\left[ \text{CH} - \text{CH}_2 \right]_q$ $\begin{array}{c} \text{O} \\ \parallel \\ \text{C} \\ \parallel \\ \text{O} \\ \text{Na}^{+1} \end{array}$
	Polysulfonate ( $\text{Na}^{+1}$ salt)	$\left[ \text{CH} - \text{CH}_2 \right]_r$ $\begin{array}{c} \text{O} = \text{S} - \text{O} \\   \\ \text{O}^{-1} \\ \text{Na}^{+1} \end{array}$
AMPS	2-Acrylamido-2-methylpropanesulfonic Acid	$\left[ \text{CH}_2 - \underset{\begin{array}{c} \text{C} = \text{O} \\   \\ \text{N} - \text{H} \\   \\ \text{CH}_3 - \text{C} - \text{CH}_3 \\   \\ \text{CH}_2 \\   \\ \text{O} = \text{S} - \text{O} \\   \\ \text{O}^{-1} \\ \text{Na}^{+1} \end{array}}{\text{CH}} \right]_s$

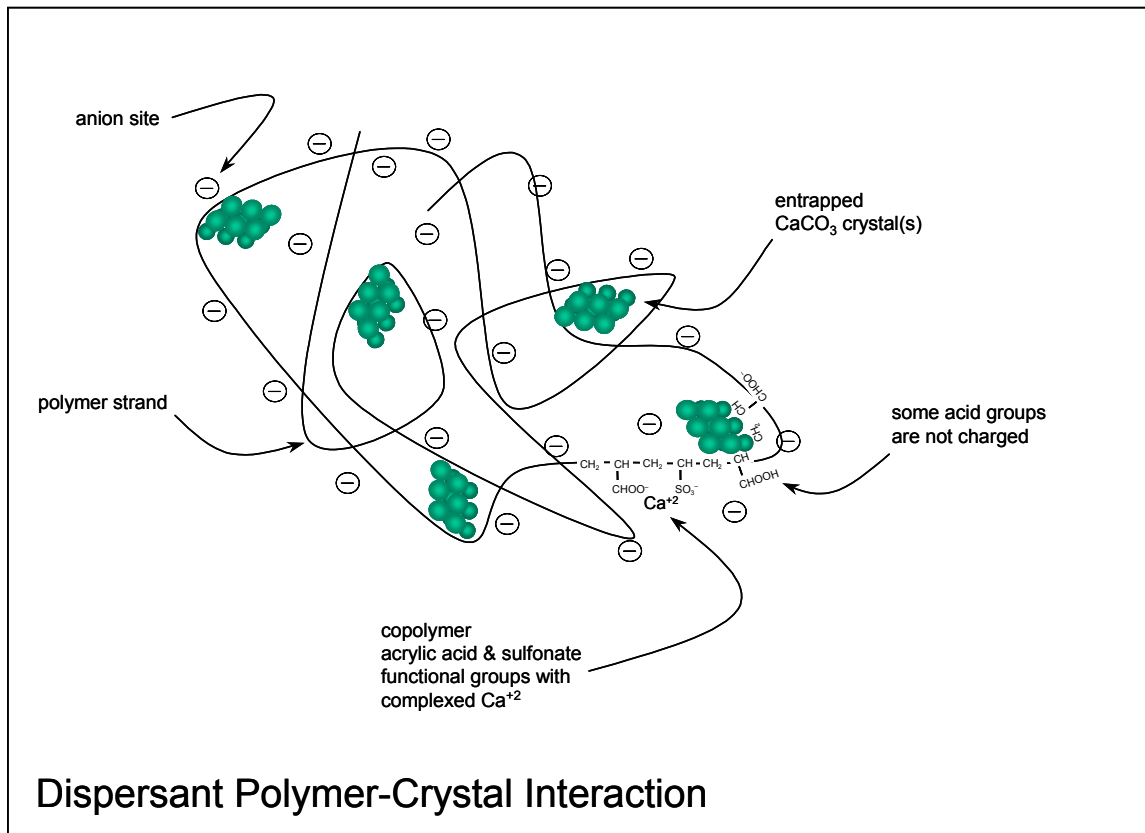


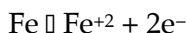
Figure 5-1.

### 5.3.1. Mild Steel Corrosion

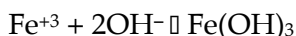
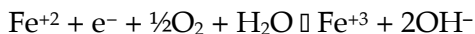
Mild steel corrosion can be a significant problem in oxygen-rich cooling systems. As stated above, specialty chemicals are used to inhibit mild steel corrosion by protecting wetted surfaces with a protective film. Carbon steel corrosion can start where there is a microscopic surface abnormality such as a gouge or scratch that interrupts the natural protective oxide film (known as *magnetite*). Other forms of corrosion can be initiated under deposits found on metal surfaces, within crevices formed by metal components, or within microbiological deposits. Note, the following discussion describes a simplified corrosion mechanism; there are numerous conditions and environments that initiate corrosion.

The corrosion process starts with a loss of electrons at a surface abnormality on the metal—this area of the metal is known as the anode. Electrons generated by the anodic reaction are transported via the conductive solution comprised of dissolved salts in water to a cathodic site where iron oxides are formed. Oxygen, which plays an important role in this reaction, is reduced to hydroxyl ions, which in turn react with dissolved iron to form iron oxide (rust) (Lisin and Laronge 1993). Refer to the following reaction sequences:

### Anodic Reaction



### Cathodic Reactions



Specialty chemicals are used to prevent corrosion by physically interrupting the flow of electrons from the anode to the cathode via an insulating film. There are two types of mild steel corrosion inhibitors—anodic and cathodic. As the names imply, anodic inhibitors insulate the anode portion of the corrosion cell and cathodic inhibitors the cathode. Some examples of anodic inhibitors include: chromate, molybdate, nitrite, orthophosphate, polysilicate, and orthosilicate. Cathodic inhibitors include: polyphosphate, zinc, molybdate, orthophosphate, and polysilicate. As can be noted, some inhibitors are multifunctional. Many inhibitors that once were considered “standard treatment” are not used today because of strict environmental rules, e.g., chromate is prohibited by the EPA for use in open cooling systems (EPA 2002). Zinc, nitrite, and molybdate are generally not permitted in California.

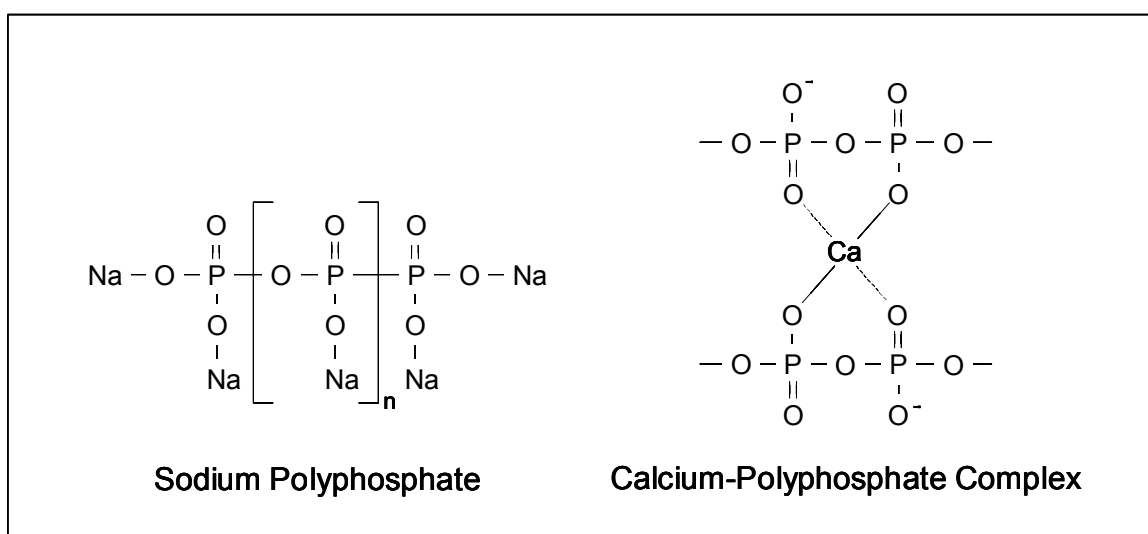
Depending on the specialty chemical used to prevent the corrosion of mild steel, a protective layer must be established. The layer can be composed of calcium carbonate, polyphosphate and calcium carbonate, calcium carbonate and calcium phosphate, etc. The simplest and oldest form of protection against mild corrosion involves pH control in the presence of alkalinity and calcium to induce a protective film of calcium carbonate ( $\text{CaCO}_3$ ) over wetted metal surfaces. This form of protection was initially practiced in the early 1900s (Langelier published the calculation methodology for the LSI in 1936). Conditions for  $\text{CaCO}_3$  controlled deposition are commonly monitored by the LSI, which utilizes a simple index calculation to measure the calcium carbonate saturation of the bulk cooling water (refer to Section 2, Indices and Guidelines). A protective film of calcium carbonate will be established over wetted surfaces under certain conditions of pH, alkalinity, calcium hardness, temperature, and background salt content. The formation of corrosion cells and the transfer of electrons that act to solubilize iron and perpetuate corrosion are physically blocked by the protective film.

Polyphosphates have also been used for a number of years to inhibit the corrosion of mild steel (World Health Organization 2001). Polyphosphates are polymerized chains of sodium phosphate that blanket metal surfaces by chemically bonding to deposited calcium carbonate films and calcium ions in solution. The resulting film consists of a calcium carbonate layer covered with a sheet-like layer of calcium-complexed polyphosphate. Refer to Figure 5-2 for a representation of sodium polyphosphate and the calcium-polyphosphate complex.

In addition to insulating the wetted iron surface from oxygenated water and conductive electrolytes (salts in solution), the fused calcium carbonate/calcium polyphosphate film also prevents further deposition by distorting calcium carbonate crystal growth on the bulk-water

side of the film. The concentration of polyphosphates in solution can be used to regulate the overall thickness of the protective film.

Polyphosphates can also degrade to orthophosphate in the presence of oxidizing biocides. Orthophosphates generated by the degradation of polyphosphates (as well as phosphonates) can also be utilized to supplement the calcium carbonate protective layer. At iron oxide corrosion sites, the pH is slightly elevated at the anode with the formation of  $\text{OH}^-$ . Oxygen reacts with electrons released at the corrosion cell forming  $\text{OH}^-$  and elevates the pH around the cell. (Lisin and Laronge 1993) Even if bulk water pH is kept low (e.g., 7.0), local pH can be elevated because of localized formation of  $\text{OH}^-$  at the corrosion cell. Therefore, at corrosion sites, a significant fraction of orthophosphate will be converted to  $\text{PO}_4^{3-}$ , and will readily react with calcium and iron ions to blanket active cells.



**Figure 5-2. Sodium polyphosphate and the calcium-polyphosphate complex**

### 5.3.2. Copper Corrosion

Copper alloys are successfully protected by a family of compounds known as azoles. Tolytriazoles (TTA) are the most common form of this compound. The mechanism of protection is similar to that of iron (discussed previously) in that a physical barrier forms over a corrosion cell to inhibit the flow of electrons from the anode. Tolytriazoles (even at low doses of 2 to 3 mg/l) form a tenacious bond to the surface of copper alloys. A protective film is then established which can dramatically reduce copper corrosion. Refer to Figure 5-3 for a representation of the tolytriazole protective film mechanism.

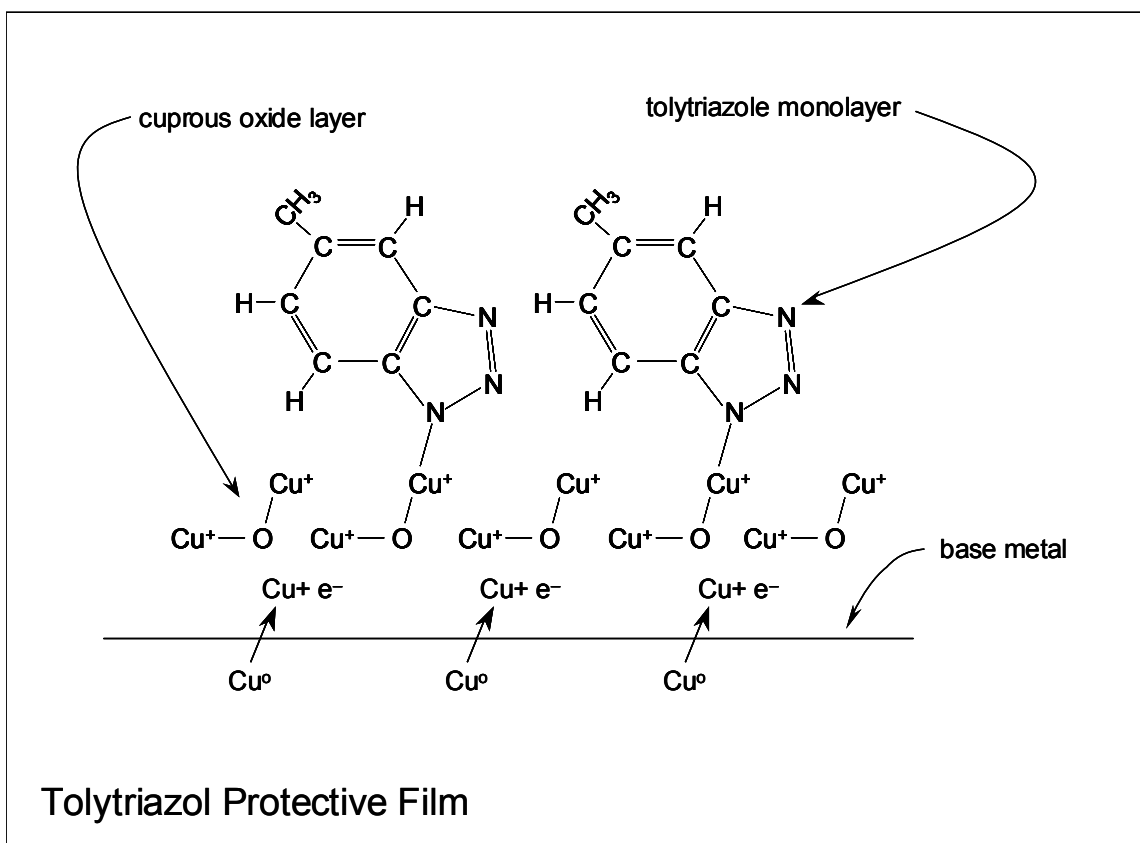


Figure 5-3. The polytriazole protective film mechanism

## 6.0 Source Water Chemistry

### 6.1. Introduction

Water chemistry is the starting point for evaluating potential source waters for power plant cooling. The information provided in most water analyses must be converted to functional concentration units, weak acids require speciation, and the cation and anions must be balanced before the water chemistry can be evaluated for cooling water use. This section outlines procedures to review, modify, and prepare source water chemistry for analysis.

The tables and worksheets provided in this section (and subsequent sections of this report) contain example data, so that readers may better follow the flow of the calculations. Readers can use these tables and worksheets for their own calculations by replacing the example data with their own site-specific data. The Excel water quality calculator performs all of the calculations found in this section, as well as those discussed in Section 7 of this report.

### 6.2. $\text{CaCO}_3$ Molar Equivalents

When evaluating cooling system chemistry, molar equivalent concentrations are used to predict ionic interactions (also used in other types of water treatment evaluations). For example, using weight-based concentrations, 4.12 mg/l of magnesium ( $1 \times 10^{-4}$  molar equivalents of  $\text{Mg}^{+2}$  ions) will react with 1.04 mg/l of sulfate ( $1 \times 10^{-4}$  molar equivalents of  $\text{SO}_4^{-2}$  ions) to form a  $\text{MgSO}_4$  ion association. If we convert these concentrations to calcium carbonate molar equivalents, then 1.00 mg/l of magnesium expressed as a calcium carbonate ( $\text{CaCO}_3$ ) equivalent will react with 1.00 mg/l of sulfate expressed as a calcium carbonate equivalent. The units for calcium carbonate equivalents are typically expressed as mg/l $_{\text{CaCO}_3}$ . Using “one-to-one” calcium carbonate molar equivalents permits ionic reactions as well ionic neutrality relationships to be determined easily and accurately.

Another important area, where equivalents are used in cooling water assessment, is the determination of electroneutrality of the ions in water. When a water analysis is prepared for a cooling water assessment, ions are usually organized by valence groups—cations and anions—where valence is the charge of the ion. Cations have a positive charge and anions a negative charge. In nature, ions in solution are always in balance (i.e., the total ionic charge imposed by cations is equal to the total charge of anions). However, in practice, many water analyses prepared by commercial laboratories do not “balance” the analytical results to observe electroneutrality (although many check results for electroneutrality).

To check electroneutrality, the sum of the calcium carbonate molar equivalents of cations must be equal to the sum of the anion calcium carbonate molar equivalents. Typically, to correct electroneutrality, either the sodium or chloride concentration (or both) is adjusted to bring the analysis to balance. Note, if the analysis is significantly off (i.e., the ratio of total cations to total anions is greater than 1.1 or less than 0.9), the analysis is flawed and should be re-run. An electroneutrality test is also a good quality control check for any water analysis.

The calcium carbonate standard was adopted many years ago and is used industrywide. The standard evolved out of early work with calcium carbonate scale and solubility studies. Sometimes molar equivalents are used—expressed as milliequivalents per liter (meq/l)—but this convention is rare in cooling system evaluations. Refer to Table 6-1 for common  $\text{CaCO}_3$  conversion factors.

**Table 6-1. Common CaCO<sub>3</sub> Conversion Factors**

Ion	Symbol	Molecular Weight	Conversion Factor
Sodium	Na <sup>+1</sup>	23.0	2.17
Potassium	K <sup>+1</sup>	39.1	1.28
Calcium	Ca <sup>+2</sup>	40.1	2.50
Magnesium	Mg <sup>+2</sup>	24.3	4.12
Ammonium	NH <sub>4</sub> <sup>+1</sup>	17.0	2.78
Bicarbonate	HCO <sub>3</sub> <sup>-1</sup>	61.0	0.82
Carbonate	CO <sub>3</sub> <sup>-2</sup>	60.0	1.67
Carbon Dioxide	CO <sub>2</sub>	44.0	1.14
Chloride	Cl <sup>-1</sup>	35.5	1.41
Sulfate	SO <sub>4</sub> <sup>-2</sup>	96.1	1.04
Phosphate	PO <sub>4</sub> <sup>-3</sup>	95.0	1.58
Monophosphate	HPO <sub>4</sub> <sup>-2</sup>	96.0	1.04
Biphosphate	H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup>	97.0	0.52

The conversion factor is calculated as follows:

$$\text{Conversion Factor} = \frac{50 \times \text{Abs}(\text{valence})}{MW} \quad (28)$$

Where *Abs(valence)* is the absolute value of the valence of the ion and *MW* is its molecular weight. Magnesium has a valence of +2 and its molecular weight is 24.3 grams per mole, and sulfate has a valence of -2 and its molecular weight is 96.1 grams per mole. Applying these values to the above formula, the conversion factor for Mg<sup>+2</sup> is 4.12, and for SO<sub>4</sub><sup>-2</sup>, it is 1.04.

Carbon dioxide is an exception to the conversion factor rule since it does not have a charge. By convention, carbon dioxide is treated as a monovalent ion (its valence equals -1), because in alkalinity reactions it behaves as such.

### 6.3. Preparing Source Water Chemistry

To evaluate any source water, the data must first be balanced ionically to achieve electroneutrality and put into a standard format. Most chemical analyses prepared by commercial laboratories are provided in a variety of formats and almost always require



reformatting. In California, potable water purveyors must provide an annual report of water quality, which includes a significant amount of information, but usually is inadequate for cooling system analysis—often missing are critical constituents such as silica. Municipal wastewater treatment plants also report effluent quality as required by discharge permits and usually do not report constituents such as sodium, potassium, calcium, magnesium, chloride, sulfate, nitrate, and silica.

The following procedures should be used to standardize units of concentration, speciate constituents and balance a source water chemical analysis to electroneutrality.

### **6.3.1. Formatting Source Water Chemistry**

In this section, a sample water analysis is used to illustrate the process required to format a source water chemistry for cooling system evaluation. The source water analysis is tertiary treated effluent from a municipal wastewater treatment plant in the San Francisco Bay Area. Reclaimed water is also referred to as Title 22 Water (from the California Code of Regulations). Refer to Table 6-2 for the analysis. Note that the format of Table 6-2 can be used for any source of water being considered for cooling tower make-up.

The constituents identified in Table 6-2 will be used to determine electroneutrality and speciate critical components in the water. Care should be taken to note the units of concentration, because a number of conventions are used. For example, alkalinity is usually reported as  $\text{mg/l}_{\text{CaCO}_3}$ . Sometimes only bicarbonate alkalinity,  $\text{HCO}_3^{-1}$ , is reported as  $\text{mg/l}_{\text{CaCO}_3}$ . It can be reported as M alkalinity, which is total alkalinity (all species) as  $\text{mg/l}_{\text{CaCO}_3}$ . Ammonia, nitrate, and nitrite are usually reported as  $\text{mg/l}_\text{N}$ . Phosphate can be reported as total phosphorous ( $\text{mg/l}_\text{P}$ ) or orthophosphate ( $\text{mg/l}_{\text{PO}_4}$ ).

Enter the values for  $\text{Na}^{+1}$ ,  $\text{K}^{+1}$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Cl}^{-1}$ , and  $\text{SO}_4^{-2}$  from Table 6-2 into Table 6-3. Alkalinity, ammonia, and phosphates will be speciated and nitrate, nitrite, and silica converted to species-based concentration values as required. At the conclusion of this section, the data will be summarized and ready for analysis.

Lastly, data such as turbidity—which is somewhat subjective and not directly useable in cooling system calculations—should be noted. Highly turbid water may require pretreatment. Also, parameters for organic constituents, heavy metals, color, odor, etc. should also be noted, and depending on the situation, may require additional treatment. Such treatment is not within the scope of this document.

**Table 6-2. Source Water Chemistry – Reported Data**

	Reported Data	Units (1)
Na <sup>+1</sup>	116	mg/l <sub>Na</sub>
K <sup>+1</sup>	12.5	mg/l <sub>K</sub>
Ca <sup>+2</sup>	32.6	mg/l <sub>Ca</sub> (2)
Mg <sup>+2</sup>	15.5	mg/l <sub>Mg</sub> (2)
Total Alkalinity	204	mg/l <sub>CaCO3</sub> (3)
Cl <sup>-1</sup>	118	mg/l <sub>Cl</sub>
SO <sub>4</sub> <sup>-2</sup>	125	mg/l <sub>SO4</sub>
NO <sub>3</sub> <sup>-1</sup>	0.7	mg/l <sub>N</sub> (4)
NO <sub>2</sub> <sup>-1</sup>	1.4	mg/l <sub>N</sub> (5)
SiO <sub>2</sub>	16	mg/l <sub>SiO2</sub> (6)
NH <sub>3</sub>	18	mg/l <sub>N</sub>
Total/Ortho PO <sub>4</sub>	1.9	mg/l <sub>P</sub> (7)
TDS	484	mg/l
pH	7.5	----

**Notes**

1. Common units – always note units prior to any analysis
2. Sometimes reported as mg/l<sub>CaCO3</sub>
3. Sometimes reported separately as HCO<sub>3</sub><sup>-1</sup> and CO<sub>3</sub><sup>-2</sup> mg/l<sub>CaCO3</sub>
4. Sometimes reported as mg/l<sub>NO3</sub>
5. Sometimes reported as mg/l<sub>NO2</sub>
6. Sometimes reported as mg/l<sub>Si</sub>
7. Sometimes reported as mg/l<sub>PO4</sub>

### 6.3.2. Alkalinity Speciation

The alkalinity components—HCO<sub>3</sub><sup>-1</sup>, CO<sub>3</sub><sup>-2</sup>, and CO<sub>2</sub>—are usually provided in source water analyses as one value—either Total or M alkalinity expressed as mg/l<sub>CaCO3</sub>. M is an abbreviation for methyl orange, which is a titrating agent used to determine M alkalinity. Refer to Figure 6-1 for the relationship of carbonate alkalinity components versus pH. Acid equilibrium constants provided by Stumm (1970) and EPRI (1982) are utilized throughout this section of the report. Figures 6-2 and 6-3, which will be used to calculate CO<sub>3</sub><sup>-2</sup> and CO<sub>2</sub> concentrations, show how the carbonate and carbon dioxide molar fractions vary with respect

to pH and TDS (ionic strength). Weak acid concentrations are strongly influenced by pH, and to a lesser extent, by ionic strength.

When speciating weak acid constituents, it is easier and more accurate to determine the smallest fractions first and calculate the larger fraction by difference, because, as can be seen from Figure 6-1, the  $\text{HCO}_3^{-1}$  fraction is asymptotic to 1.0 in the pH range of most source waters. Refer to Equation 29 for a description of this estimating relationship.

$$MF_{\text{HCO}_3^{-1}} = 1 - MF_{\text{CO}_2} - MF_{\text{CO}_3^{-2}} \quad (29)$$

For the sample water source, at a pH of 7.5 and TDS of 484 mg/l, the molar fraction ( $MF_{\text{Specie}}$ ) of  $\text{CO}_3^{-2}$  is approximately  $1.7 \times 10^{-3}$  from Figure 6-2 and  $\text{CO}_2$  is  $4 \times 10^{-2}$  from Figure 6-3. The molar fraction of  $\text{HCO}_3^{-1}$  is calculated by difference to be 0.958, using Equation 29. Enter these values in the Carbonate Alkalinity Speciation Worksheet below.

To calculate the concentration of each component, multiply the total alkalinity (which is expressed as mg/l $\text{CaCO}_3$ ) by the molar fraction of each component. Note that concentrations expressed as mg/l $\text{CaCO}_3$  are molar equivalent concentrations; therefore, the molar fractions can be used directly without modification. At a total (M) alkalinity of 204 mg/l $\text{CaCO}_3$ , the concentration of the components would be: 195.4 mg/l $\text{CaCO}_3$  of  $\text{HCO}_3^{-1}$  (204 mg/l $\text{CaCO}_3$  of total alkalinity  $\times$  0.929), 0.4 mg/l $\text{CaCO}_3$  of  $\text{CO}_3^{-2}$ , and 8.2 mg/l $\text{CaCO}_3$  of  $\text{CO}_2$  (rounding values may make the total speciated concentration slightly higher or lower than the starting concentration). Enter the data into column B of Table 6-3.

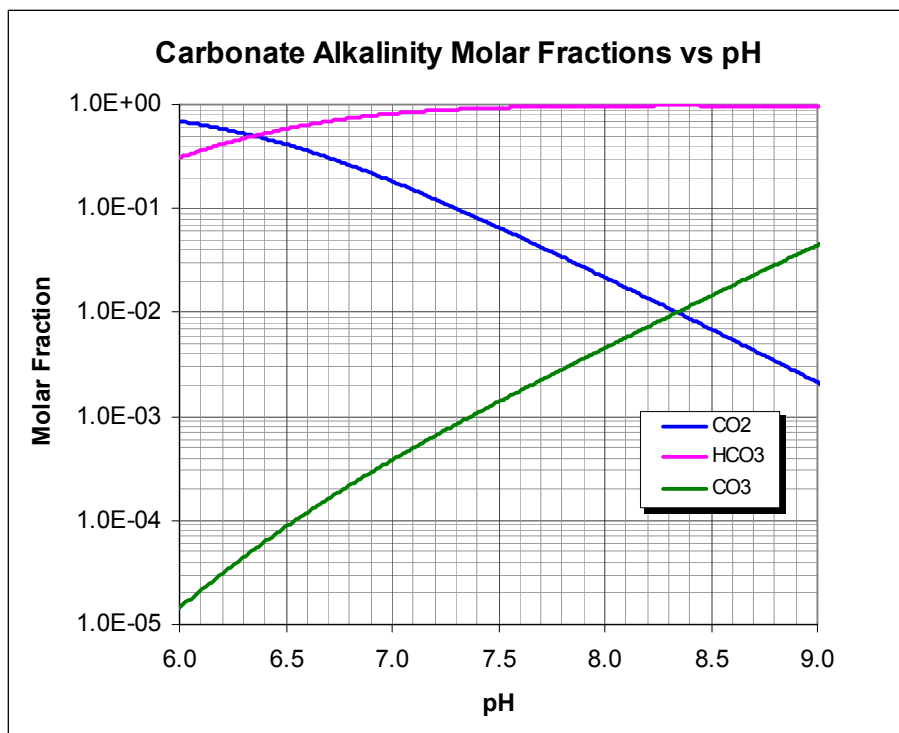


Figure 6-1.

# Carbonate Alkalinity Speciation Worksheet

	A	B	C
Carbonate	Reported		Speciated
Specie	Data (1) mg/l <sub>CaCO3</sub>	Molar Fraction (2)	Data mg/l <sub>CaCO3</sub> (C=AxB)
HCO <sub>3</sub> <sup>-1</sup>	----	0.958 (3)	195.4
CO <sub>3</sub> <sup>-2</sup>	----	1.7x10 <sup>-3</sup>	0.4
CO <sub>2</sub>	----	4x10 <sup>-2</sup>	8.2
Total	204	----	204.0

## Notes

1. Total Alkalinity from Table 6-2.
2. Molar fractions from Figures 6-1 and 6-2.
3. Calculated by difference – refer to Equation 29.

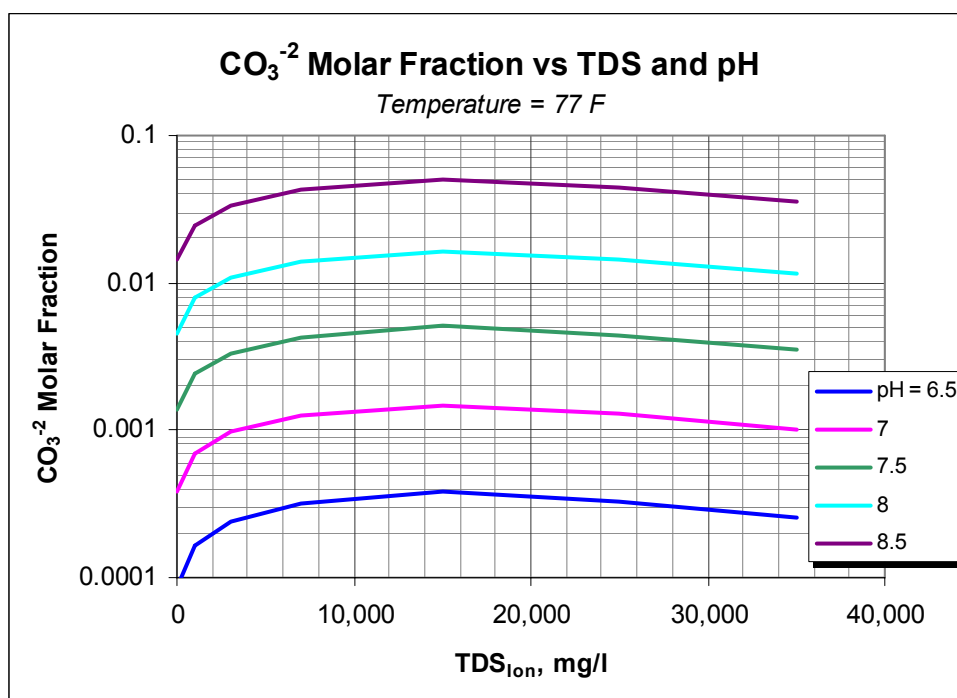
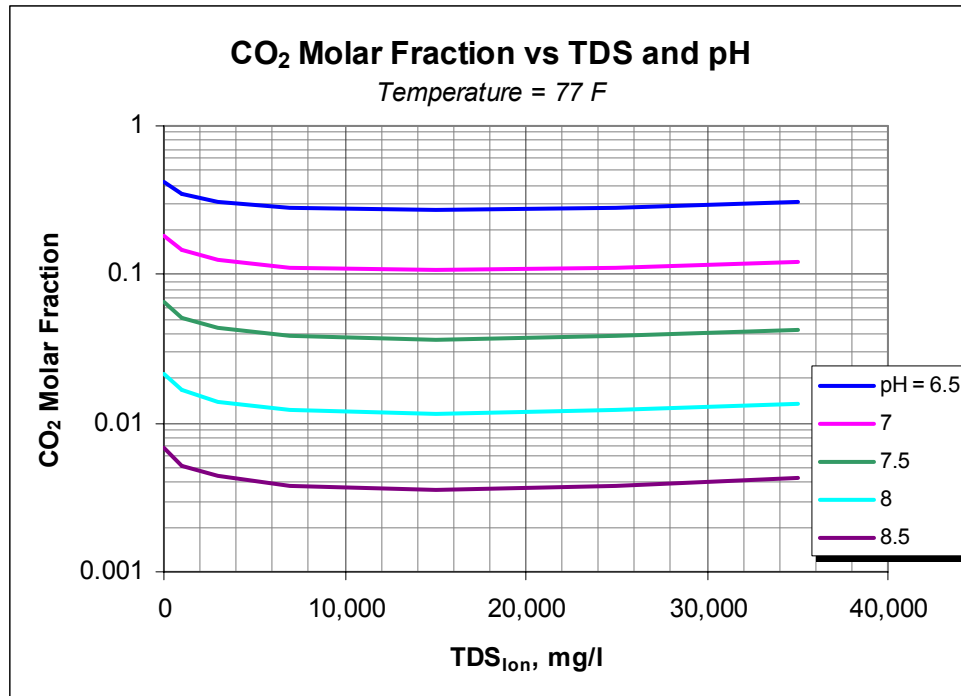


Figure 6-2.



**Figure 6-3.**

### 6.3.3. Ammonia Speciation

Ammonia concentrations are usually provided as mg/l<sub>N</sub> (nitrogen equivalents). The use of nitrogen equivalents is common in municipal wastewater treatment, because it simplifies certain conversion calculations used to predict biological reactor performance.

To speciate ammonia, refer to Figures 6-4 and 6-5 and the Ammonia Speciation Worksheet below. At a source water pH of 7.5, the molar fraction of NH<sub>3</sub> is 1.8x10<sup>-2</sup>. NH<sub>4</sub><sup>+</sup> is calculated by difference to be 0.982. Again, the speciation analysis is started by reading the smallest values first (from either Figure 6-4 or 6-5).

Speciation fraction adjustments are not required for ammonia. Activity coefficients, which are effected by ionic strength (TDS), “cancel out” in the ammonia speciation analysis. For a total reported ammonia of 18 mg/l<sub>N</sub>, the concentration of NH<sub>4</sub><sup>+</sup> is 17.7 mg/l<sub>N</sub>, and NH<sub>3</sub> is 0.3 mg/l<sub>N</sub>.

To convert the nitrogen-equivalent concentrations to NH<sub>4</sub><sup>+</sup> (mg/l<sub>NH4</sub>) and NH<sub>3</sub> (mg/l<sub>NH3</sub>), multiply the speciated values by 1.29 and 1.21, respectively, to obtain 22.8 mg/l<sub>NH4</sub> and 0.36 mg/l<sub>NH3</sub>. The conversion factors—1.29 and 1.21—are simply the ratios of the molecular weight of NH<sub>4</sub><sup>+</sup> to N (18/14) and NH<sub>3</sub> to N (17/14), respectively. Enter the data into column B of Table 6-3.

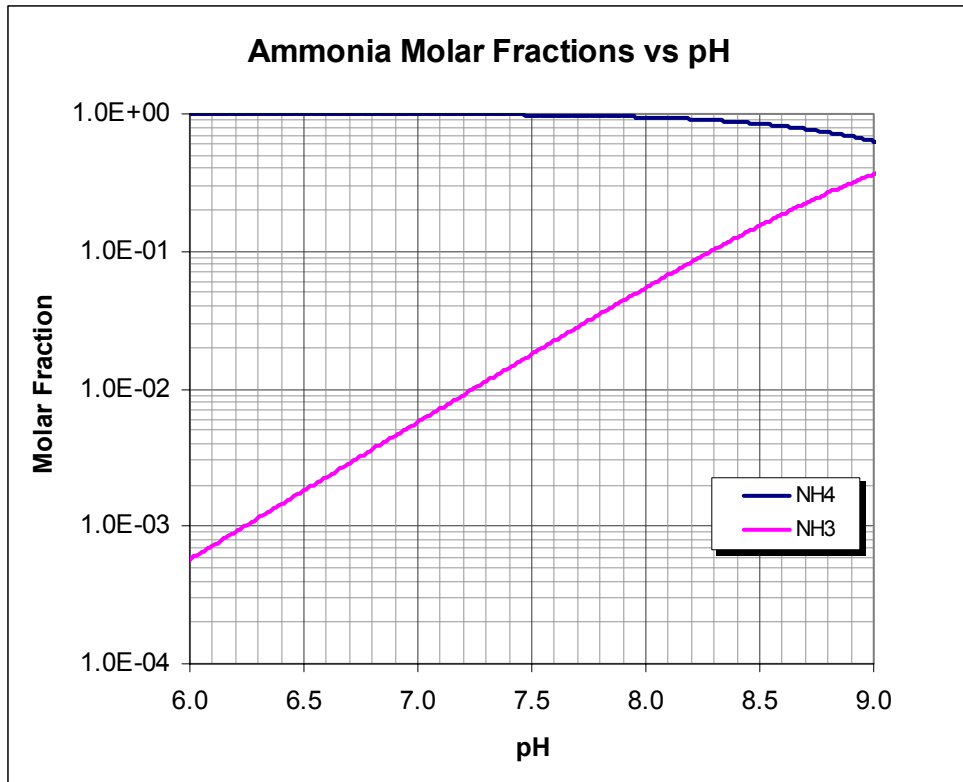


Figure 6-4.

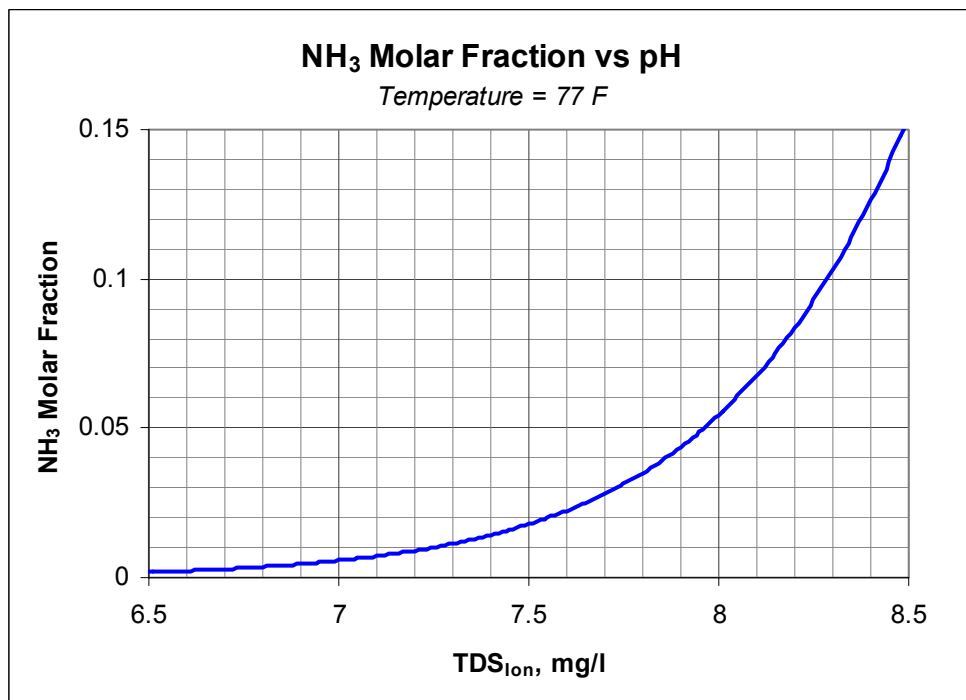


Figure 6-5.

### Ammonia Speciation Worksheet

	A	B	C	D	E
	Reported		Speciated		Speciated
Ammonia	Data (1)	Molar	Data	Conversion	Data
Specie	mg/l <sub>N</sub>	Fraction (2)	mg/l <sub>N</sub> (C=AxB)	Factor (3)	mg/l <sub>Specie</sub> (E=CxD)
NH <sub>4</sub> <sup>+1</sup>	N/A	0.982 (4)	17.7	1.29	22.8
NH <sub>3</sub>	18	1.8x10 <sup>-2</sup>	0.3	1.21	0.36

#### **Notes**

1. Total ammonia from Table 6-2.
2. Molar fractions from Figures 6-4 and 6-5.
3. Ratio of molecular weight of NH<sub>4</sub><sup>+1</sup> to N (18/14) and NH<sub>3</sub> to N (17/14).
4. NH<sub>4</sub><sup>+1</sup> fraction calculated by difference.

#### **6.3.4. Phosphate Speciation**

Phosphate concentrations are reported either as mg/l<sub>P</sub> or mg/l<sub>PO<sub>4</sub></sub> and are designated as *orthophosphate* in water quality analyses (sometimes designated as *total phosphate* or just *phosphate*). Orthophosphate is a non-organic/non-polymerized form of phosphate, and in degraded water (e.g., reclaimed municipal effluent), orthophosphate is usually the most prominent form of phosphorous compounds.

For the purpose of speciation, convert the orthophosphate concentration to mg/l<sub>P</sub> (if they are not already in that form)—this conversion will allow the speciation to be conducted as phosphorous molar equivalents. Multiply mg/l<sub>PO<sub>4</sub></sub> by 0.326 to obtain mg/l<sub>P</sub>—the ratio of the molecular weight of P to PO<sub>4</sub> (31/95). Refer to Figure 6-6, Phosphate Molar Fractions versus pH, to speciate phosphate. Figures 6-7, 6-8, and 6-9 show the molar fractions of the minor phosphate components—H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>PO<sub>4</sub><sup>-1</sup>, and PO<sub>4</sub><sup>-3</sup> versus pH and TDS.

As with the above examples, at a pH of 7.5 and TDS of 484 mg/l, the molar fraction of H<sub>3</sub>PO<sub>4</sub> is 1.0x10<sup>-6</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-1</sup> is 2.5x10<sup>-1</sup>, and PO<sub>4</sub><sup>-3</sup> is 1.3x10<sup>-5</sup>. Again, start the speciation analysis by reading from Figures 6-7, 6-8, and 6-9. Enter the data in the Phosphate Speciation worksheet below. The molar fraction of HPO<sub>4</sub><sup>-2</sup> is calculated by difference.

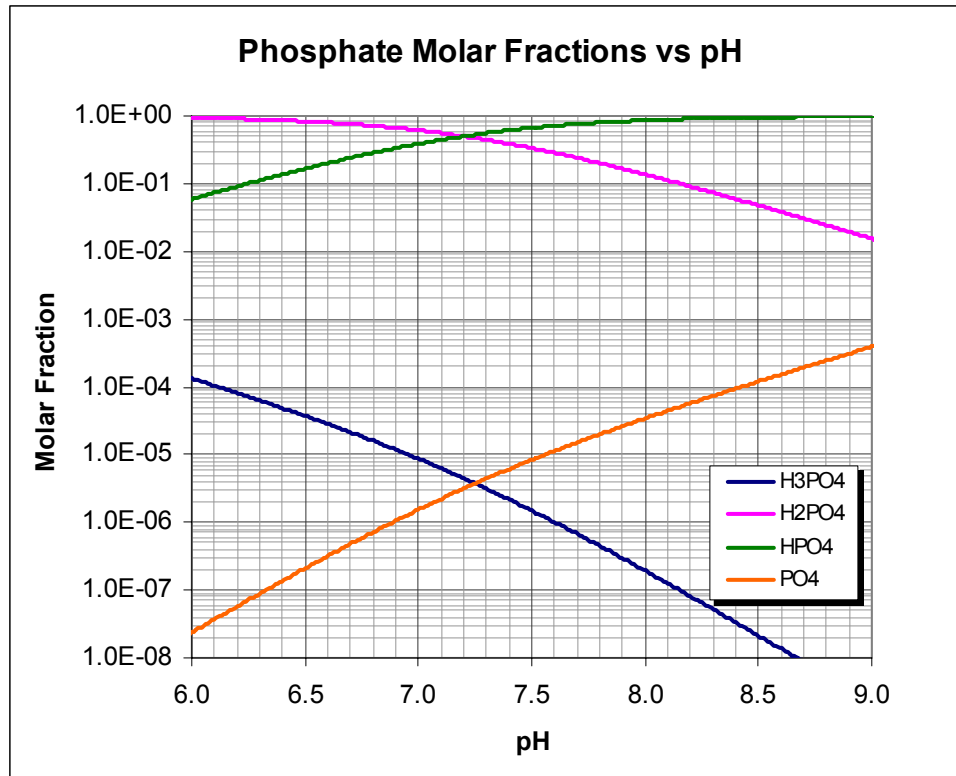


Figure 6-6.

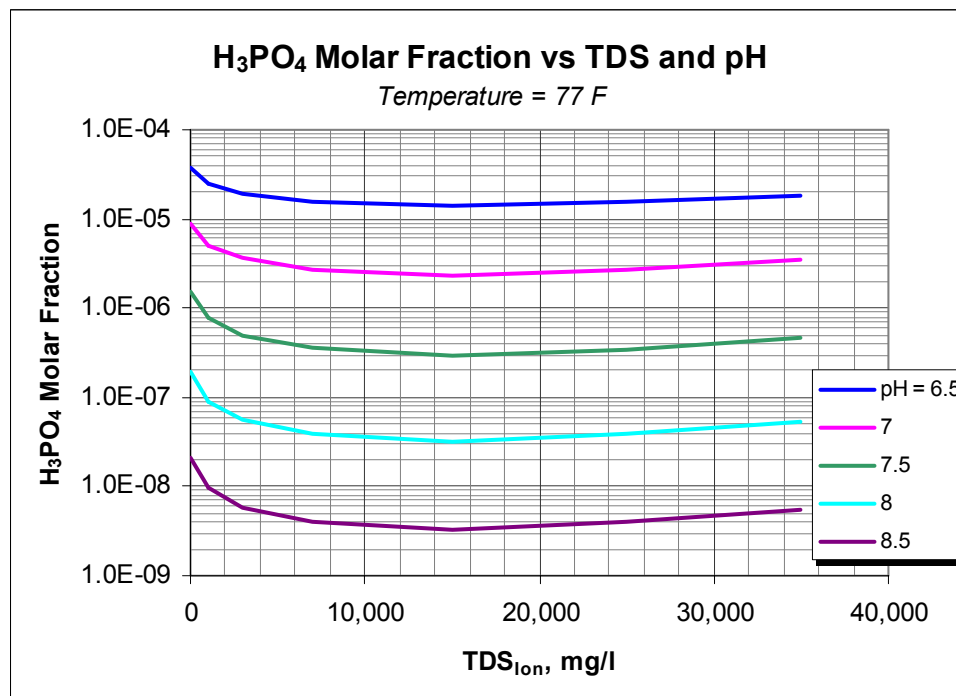


Figure 6-7.



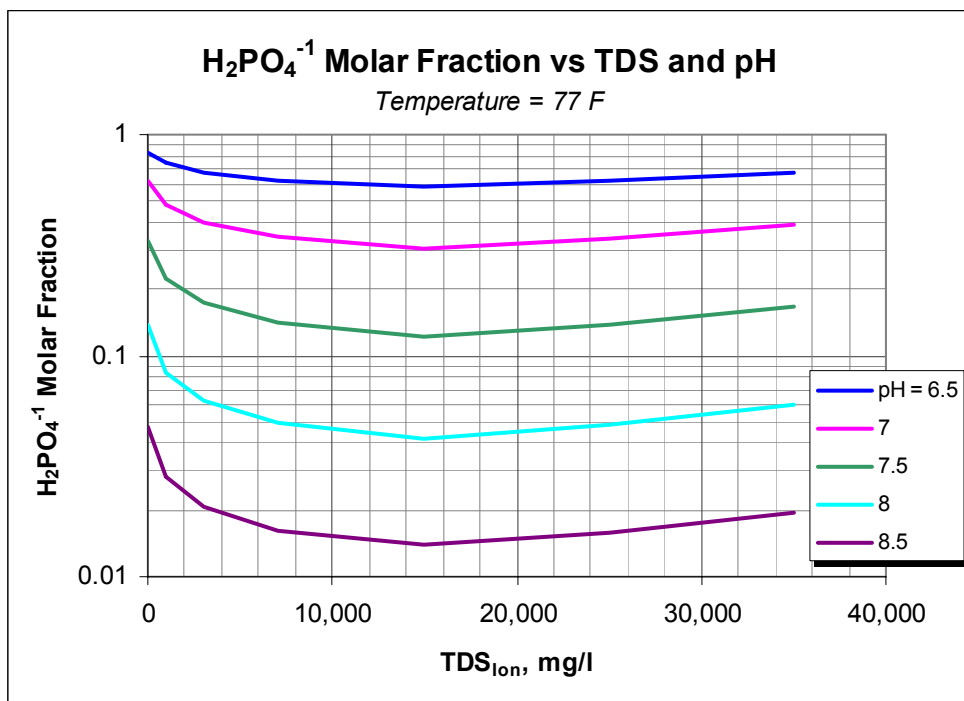


Figure 6-8.

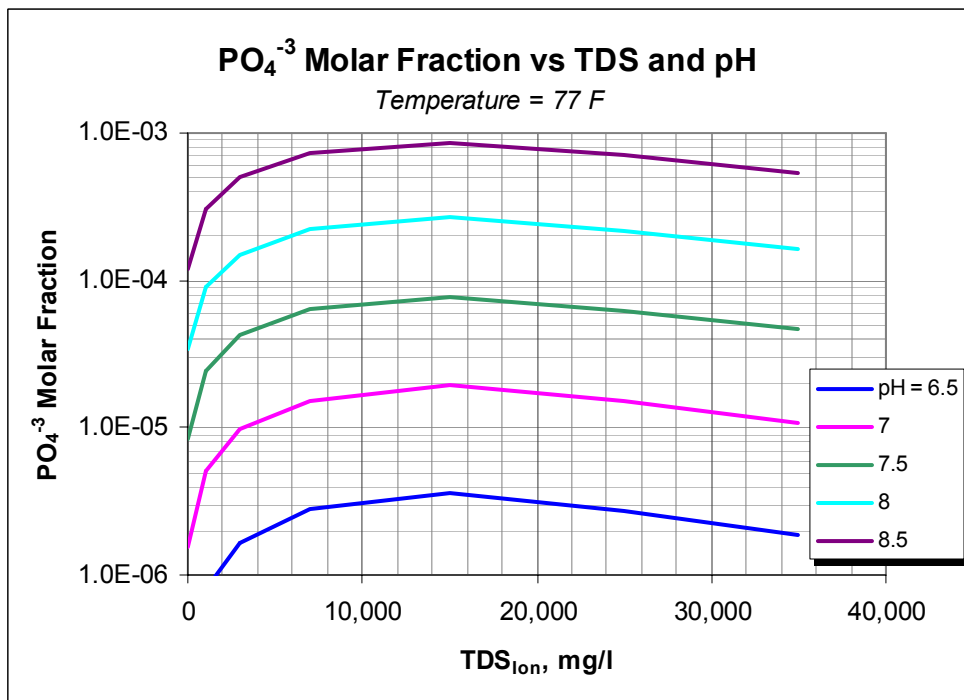


Figure 6-9.

Using the molar fractions, calculate the equivalent concentrations of the phosphate species, all expressed as mg/l<sub>P</sub>. Calculate the speciated concentrations for orthophosphate by multiplying by the conversion factors provided in the worksheet. Enter the data into column B of Table 6-3.

Phosphate Speciation Worksheet

	A	B	C	D	E
Phosphate Specie	Reported Data (1) mg/l <sub>P</sub>	Molar Fraction (2)	Speciated Data mg/l <sub>P</sub> (C=AxB)	Conversion Factor	Speciated Data mg/l <sub>Specie</sub> (E=CxD)
H <sub>3</sub> PO <sub>4</sub>	----	1.0x10 <sup>-6</sup>	1.90x10 <sup>-6</sup>	3.16	6.00x10 <sup>-6</sup>
H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup>	----	0.25	0.48	3.13	1.50
HPO <sub>4</sub> <sup>-2</sup>	----	0.75 (4)	1.42	3.10	4.40
PO <sub>4</sub> <sup>-3</sup>	----	1.3x10 <sup>-5</sup>	2.47x10 <sup>-5</sup>	3.06	7.56x10 <sup>-5</sup>
Ortho-PO <sub>4</sub>	1.9	----	1.90	----	----
<b>Notes</b> 1. Ortho-PO <sub>4</sub> from Table 6-2. 2. Molar fractions from Figure 6-5. 3. Adjustment factors from Figures 6-6, 6-7, and 6-8. 4. H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup> calculated by difference. 5. Ratio of molecular weight of H <sub>3</sub> PO <sub>4</sub> to P (98/31), H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup> to P (97/31), HPO <sub>4</sub> <sup>-2</sup> to P (96/31), and PO <sub>4</sub> <sup>-3</sup> to P (95/31).					

### 6.3.5. Other Concentration Conversions

The Miscellaneous Conversions worksheet is provided for converting nitrate (reported as mg/l<sub>N</sub>) and nitrate (as mg/l<sub>N</sub>) and silica reported (as mg/l<sub>Si</sub>) to their specie values expressed as mg/l<sub>Specie</sub>. The conversion factors are the ratios of the molecular weight of NO<sub>3</sub><sup>-1</sup> to N (62/14), NO<sub>2</sub><sup>-1</sup> to N (46/14), and SiO<sub>2</sub> to Si (60/28).

Miscellaneous Conversions Worksheet

	A	B	C
Carbonate Specie	Reported Data	Conversion Factor	Converted Data (C=AxB)
NO <sub>3</sub> <sup>-1</sup>	mg/l <sub>N</sub>	4.43	mg/l <sub>NO3</sub>
NO <sub>2</sub> <sup>-1</sup>	mg/l <sub>N</sub>	3.29	mg/l <sub>NO2</sub>
SiO <sub>2</sub>	mg/l <sub>Si</sub>	2.14	mg/l <sub>SiO2</sub>

Using the sample water analysis, 0.7 mg/l<sub>N</sub> of nitrate would convert to 3.10 mg/l<sub>NO<sub>3</sub></sub>, and 1.4 mg/l<sub>N</sub> of nitrite would convert to 4.61 mg/l<sub>NO<sub>2</sub></sub>. Because silica was reported as mg/l<sub>SiO<sub>2</sub></sub>, this conversion calculation was not necessary.

### 6.3.6. Balancing the Data

After carbonate alkalinity, ammonia, and phosphate have been speciated and concentration conversions for nitrate, nitrite, and silica (if required) have been completed, the water balance is ready for the next step—electroneutrality check.

Using the conversion factors in Table 6-1, multiply the concentrations in column B of Table 6-3 by the appropriate conversion factor to convert all ionic concentrations to calcium carbonate equivalents, mg/l<sub>CaCO<sub>3</sub></sub>. Concentration units for ammonia (NH<sub>3</sub>), silica (SiO<sub>2</sub>), and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) do not have to be converted, because these species are not ions in water, and therefore, do not contribute to electroneutrality. Also, since bicarbonate and carbonate alkalinity are already calculated as calcium carbonate equivalents, their concentration remains the same from column B to C. Calcium carbonate equivalents are entered in column C of Table 6-3.

For the sample water, the sum of the equivalent cations in column C is 476.5 mg/l<sub>CaCO<sub>3</sub></sub> and the sum of the anions is 505.6 mg/l<sub>CaCO<sub>3</sub></sub>. Electroneutrality is not achieved with this analysis. Also, if we divide the total cations (TC) by total anions (TA), we get 0.95, which is within the criteria of 0.9 to 1.1 for an “acceptable” water analysis. Recall, if the ratio is outside of the criteria, one or more of the constituent concentrations is probably suspect, and the analysis should be repeated.

Because there is an ionic imbalance between cations and anions, adjustments will be required to achieve balance. Sodium and chloride concentrations will both be adjusted, since it is not possible to determine whether cation or anions were overstated or understated. Sodium and chloride concentrations are usually adjusted, because they are generally considered “non-reactive.” Since the total anion concentration exceeds cations by 29.0 mg/l<sub>CaCO<sub>3</sub></sub> in the sample water, the sodium and chloride concentrations will be adjusted by 14.5 mg/l<sub>CaCO<sub>3</sub></sub> (½ of the absolute difference between TC and TA). Refer to the Electroneutrality Calculation worksheet below. Using the evaluation criteria in the worksheet, Na<sup>+1</sup> is adjusted to a value of 266.2 mg/l<sub>CaCO<sub>3</sub></sub>, and Cl<sup>-1</sup> is adjusted to a value of 151.9 mg/l<sub>CaCO<sub>3</sub></sub>.

Electroneutrality Calculation	
Total Cations (TC), mg/l <sub>CaCO3</sub> (1)	476.5
Total Anions (TA), mg/l <sub>CaCO3</sub> (1)	505.5
Total Cations minus Total Anions (TC-TA), mg/l <sub>CaCO3</sub>	-29.0
Adjustment = (TC - TA)/2	-14.5
Na <sup>+1</sup> Adjustment (2)	+14.5
Adjusted Na <sup>+1</sup> = Reported Na <sup>+1</sup> + Na <sup>+1</sup> Adjustment	266.2
Cl <sup>-1</sup> Adjustment (3)	-14.5
Adjusted Cl <sup>-1</sup> = Reported Cl <sup>-1</sup> + Cl <sup>-1</sup> Adjustment	151.9
<b>Notes</b>	
1.	Values for Total Cations (TC) and Total Anions (TA) from Table 6-3 both expressed as mg/l <sub>CaCO3</sub> .
2.	Na <sup>+1</sup> adjustment is positive if TC<TA and negative if TC>TA.
3.	Cl <sup>-1</sup> adjustment is positive if TC>TA and negative if TC<TA.

**Table 6-3. Source Water Chemistry – Speciation and Electroneutrality Check**

	<b>A</b>		<b>B</b>		<b>C</b>	
	Reported (1)		Speciated		Electroneutrality Check	
	Data	Units	Data	Units	Data	Units
Na <sup>+1</sup>	116	mg/l <sub>Na</sub>	116	mg/l <sub>Na</sub>	251.7	mg/l <sub>CaCO3</sub>
K <sup>+1</sup>	12.5	mg/l <sub>K</sub>	12.5	mg/l <sub>K</sub>	16.0	mg/l <sub>CaCO3</sub>
Ca <sup>+2</sup>	32.6	mg/l <sub>Ca</sub>	32.6	mg/l <sub>Ca</sub>	81.5	mg/l <sub>CaCO3</sub>
Mg <sup>+2</sup>	15.5	mg/l <sub>Mg</sub>	15.5	mg/l <sub>Mg</sub>	63.9	mg/l <sub>CaCO3</sub>
NH <sub>4</sub> <sup>+1</sup>	N/A	N/A	22.8	mg/l <sub>NH4</sub>	63.4	mg/l <sub>CaCO3</sub>
Total Cations	N/A	N/A	N/A	N/A	476.5	mg/l <sub>CaCO3</sub>
Total Alkalinity	204	mg/l <sub>CaCO3</sub>	N/A	N/A	N/A	N/A
HCO <sub>3</sub> <sup>-1</sup>	N/A	N/A	195.4	mg/l <sub>CaCO3</sub>	195.4	mg/l <sub>CaCO3</sub>
CO <sub>3</sub> <sup>-2</sup>	N/A	N/A	0.4	mg/l <sub>CaCO3</sub>	0.4	mg/l <sub>CaCO3</sub>
Cl <sup>-1</sup>	118	mg/l <sub>Cl</sub>	118	mg/l <sub>Cl</sub>	166.4	mg/l <sub>CaCO3</sub>
SO <sub>4</sub> <sup>-2</sup>	125	mg/l <sub>SO4</sub>	125	mg/l <sub>SO4</sub>	130.0	mg/l <sub>CaCO3</sub>
NO <sub>3</sub> <sup>-1</sup>	0.7	mg/l <sub>N</sub>	3.10	mg/l <sub>NO3</sub>	2.5	mg/l <sub>CaCO3</sub>
NO <sub>2</sub> <sup>-1</sup>	1.4	mg/l <sub>N</sub>	4.60	mg/l <sub>NO2</sub>	5.0	mg/l <sub>CaCO3</sub>
H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup>	N/A	N/A	1.50	mg/l <sub>H2PO4</sub>	0.8	mg/l <sub>CaCO3</sub>
HPO <sub>4</sub> <sup>-2</sup>	N/A	N/A	4.40	mg/l <sub>HPO4</sub>	4.6	mg/l <sub>CaCO3</sub>
PO <sub>4</sub> <sup>-3</sup>	N/A	N/A	7.56x10 <sup>-5</sup>	mg/l <sub>PO4</sub>	1.19x10 <sup>-4</sup>	mg/l <sub>CaCO3</sub>
Total Anions	N/A	N/A	N/A	N/A	505.5	mg/l <sub>CaCO3</sub>
SiO <sub>2</sub>	16	mg/l <sub>SiO2</sub>	16	mg/l <sub>SiO2</sub>	16	mg/l <sub>SiO2</sub>
NH <sub>3</sub>	18	mg/l <sub>N</sub>	0.36	mg/l <sub>NH3</sub>	0.36	mg/l <sub>NH3</sub>
Ortho-PO <sub>4</sub>	1.9	mg/l <sub>P</sub>	N/A	N/A	N/A	N/A
H <sub>3</sub> PO <sub>4</sub>	N/A	N/A	6.00x10 <sup>-6</sup>	mg/l <sub>H3PO4</sub>	6.00x10 <sup>-6</sup>	mg/l <sub>H3PO4</sub>
CO <sub>2</sub>	N/A	N/A	8.2	mg/l <sub>CaCO3</sub>	8.2	mg/l <sub>CaCO3</sub>
TDS	484	mg/l	N/A	mg/l	N/A	mg/l
pH	7.5	----	7.5	----	7.5	----

**Notes**

1. Table 6-3 Incorporates all the reported source water data in Table 6-2.

### 6.3.7. Finalizing the Data

Data, which has been speciated and adjusted for electroneutrality in Table 6-3, is inserted into Table 6-4 and is ready for evaluation. The speciated and balanced data generated in Table 6-3 (Column C) comprises the first column of data in Table 6-4. The data is also converted to concentrations as specie—this conversion will allow the TDS of the water to be recalculated.

TDS is calculated by summing all the ionic and nonionic soluble species with the exception of  $\text{NH}_3$  and  $\text{CO}_2$ . Both of these constituents are considered dissolved gases (non-solids) and are not included in the calculation. Some TDS conventions also exclude ionic carbonate alkalinity constituents, because bicarbonate and carbonate decompose and volatilize as a result of gravimetric analysis (where the sample is heated in an oven and the residue is weighed); however, this convention is not used in this analysis. For completeness in the final chemical analysis, the  $\text{CO}_2$  concentration should be converted from calcium carbonate equivalents to its specie concentration.

Lastly, total concentrations for speciated constituents—total (M) alkalinity as  $\text{mg/l}_{\text{CaCO}_3}$ , total ammonia as  $\text{mg/l}_\text{N}$ , and orthophosphate as  $\text{mg/l}_\text{P}$ —are summarized at the bottom of the table. These values will be used in the next section when performing cooling tower concentration cycling calculations.

**Table 6-4. Source Water Chemistry - Speciated and Balanced**

	CaCO <sub>3</sub> Equivalents		Constituents as Specie	
	Data	Units	Data	Units
Adjusted Na <sup>+1</sup>	266.2	mg/l <sub>CaCO3</sub>	122.7	mg/l <sub>Na</sub>
K <sup>+1</sup>	16.0	mg/l <sub>CaCO3</sub>	12.5	mg/l <sub>K</sub>
Ca <sup>+2</sup>	81.5	mg/l <sub>CaCO3</sub>	32.6	mg/l <sub>Ca</sub>
Mg <sup>+2</sup>	63.9	mg/l <sub>CaCO3</sub>	15.5	mg/l <sub>Mg</sub>
NH <sub>4</sub> <sup>+1</sup>	63.4	mg/l <sub>CaCO3</sub>	22.8	mg/l <sub>NH4</sub>
Total Cations <sup>2</sup>	491.0	mg/l <sub>CaCO3</sub>	N/A	N/A
HCO <sub>3</sub> <sup>-1</sup>	195.4	mg/l <sub>CaCO3</sub>	238.4	mg/l <sub>HCO3</sub>
CO <sub>3</sub> <sup>-2</sup>	0.4	mg/l <sub>CaCO3</sub>	0.24	mg/l <sub>CO3</sub>
Adjusted Cl <sup>-1</sup>	151.9	mg/l <sub>CaCO3</sub>	107.7	mg/l <sub>Cl</sub>
SO <sub>4</sub> <sup>-2</sup>	130	mg/l <sub>CaCO3</sub>	125	mg/l <sub>SO4</sub>
NO <sub>3</sub> <sup>-1</sup>	2.5	mg/l <sub>CaCO3</sub>	3.1	mg/l <sub>NO3</sub>
NO <sub>2</sub> <sup>-1</sup>	5.0	mg/l <sub>CaCO3</sub>	4.6	mg/l <sub>NO2</sub>
H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup>	0.8	mg/l <sub>CaCO3</sub>	1.5	mg/l <sub>H2PO4</sub>
HPO <sub>4</sub> <sup>-2</sup>	4.6	mg/l <sub>CaCO3</sub>	4.4	mg/l <sub>HPO4</sub>
PO <sub>4</sub> <sup>-3</sup>	1.2x10 <sup>-4</sup>	mg/l <sub>CaCO3</sub>	7.6x10 <sup>-5</sup>	mg/l <sub>PO4</sub>
Total Anions <sup>2</sup>	491.1	mg/l <sub>CaCO3</sub>	N/A	N/A
SiO <sub>2</sub>	N/A	N/A	16	mg/l <sub>SiO2</sub>
NH <sub>3</sub>	N/A	N/A	0.36	mg/l <sub>NH3</sub>
H <sub>3</sub> PO <sub>4</sub>	N/A	N/A	6.0x10 <sup>-6</sup>	mg/l <sub>H3PO4</sub>
CO <sub>2</sub>	8.2	mg/l <sub>CaCO3</sub>	7.2	mg/l <sub>CO2</sub>
TDS	N/A	N/A	707	mg/l
pH	7.5	----	7.5	----

***Speciated Total Concentrations***<sup>(1)</sup>

Alkalinity	204	mg/l <sub>CaCO3</sub>	N/A	N/A
Ammonia	N/A	N/A	18	mg/l <sub>N</sub>
Orthophosphate	N/A	N/A	1.9	mg/l <sub>P</sub>

***Notes***

1. Values for total speciated concentrations were extracted from Table 6-2.
2. Total cations (TC) and anions (TA) expressed as mg/l<sub>CaCO3</sub> may not round to equality.

## 7.0 Site-Specific Analysis

### 7.1. Introduction

Generalized indices and water quality criteria are typically used to screen and evaluate potential water sources for cooling. Often these criteria are overly conservative, and consequently, many usable candidate waters are considered unusable. This section of the report will incorporate theory from previous chapters and will develop a procedure to analyze source water chemistry on a more realistic basis. Tools such as pH relationships, ion association, adjusted solubility constants, and the use of specialty chemicals to control acceptable scale formation will be provided to analyze the usability of water for cooling systems.

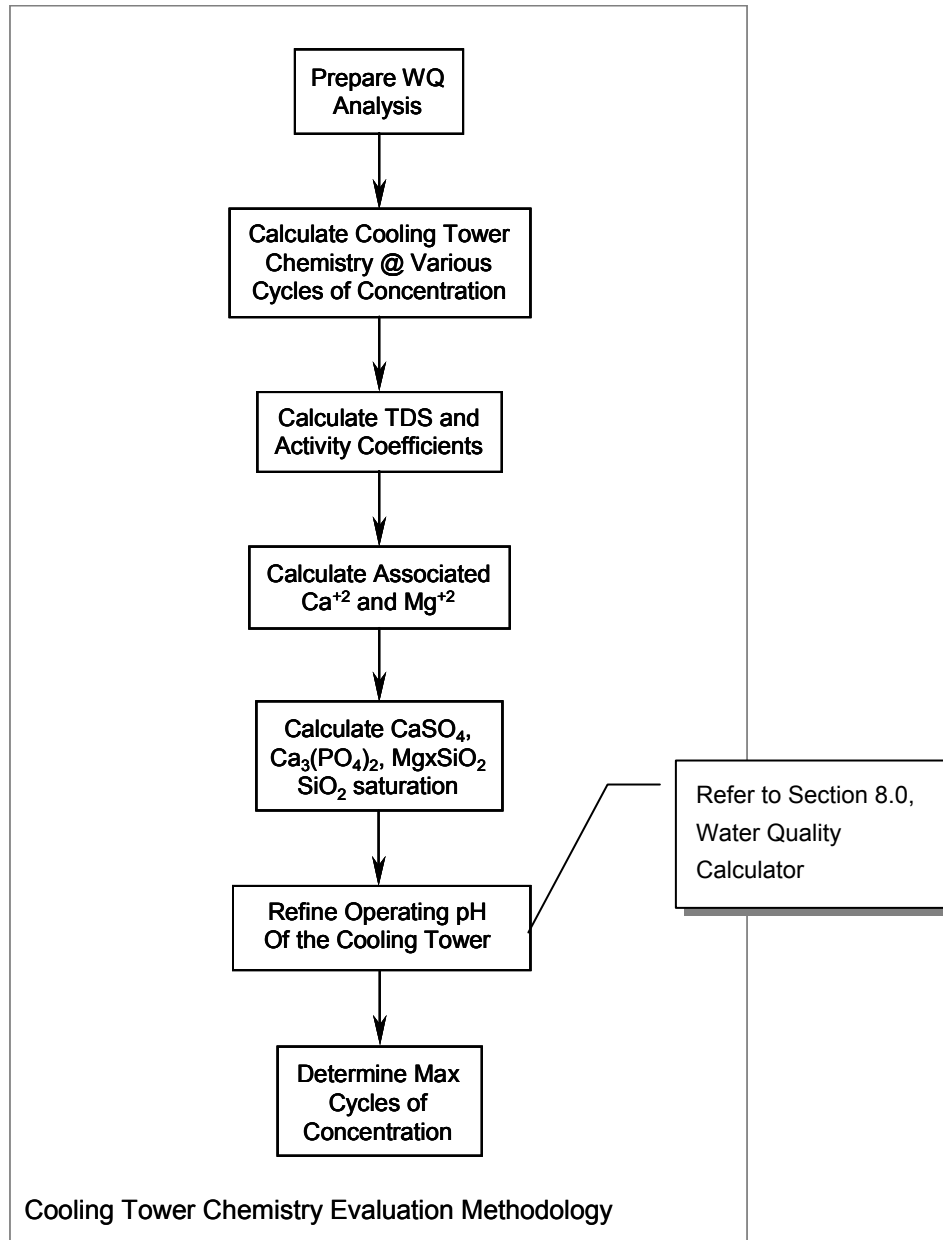
This section presents a methodology for calculating cycles of concentration for cooling systems. Figure 7-1 presents the elements of the methodology. They are outlined as follows:

1. Speciate and balance the source water for evaluation. (The methodology is outlined in Section 6, Source Water Chemistry.)
2. Calculate cooling tower chemistry at various cycles of concentration—five scenarios from 4 to 12 cycles—using a predetermined cooling system pH. This step sets the stage for detailed analysis.
3. Calculate TDS and activity coefficients. Activity coefficients will be used to adjust solubility constants.
4. Adjust calcium, magnesium, and sulfate concentrations to account for ion associations.
5. Calculate  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaHPO}_4$ ,  $\text{Mg}_2\text{Si}_3\text{O}_8 \bullet 3.5\text{H}_2\text{O}$ , and  $\text{SiO}_2$  solubility for each concentration scenario.
6. Refine the operating pH of the cooling tower. This step is important because pH will strongly effects carbonate and phosphate chemistry and thus scale (and corrosion) potential. *This type of analysis will be discussed in Section 8 using the spreadsheet calculator.*
7. Determine the maximum cycles of concentration.

The methodology is designed to evaluate cooling tower cycles of concentration for a variety of source waters with reasonable confidence. Recall that a rigorous determination of cycles of concentration would require a trial-and-error solution that is typically done with specialized software (refer to Section 4, Software). The spreadsheet calculator provided in Section 8 facilitates the theory and calculations discussed to this point in the report and in this section.

Acid equilibrium constants, ion association constants, and solubility constants provided by Stumm (1970) and EPRI (1982) are utilized throughout this section. Lastly, the specific water analysis used to illustrate calculations in Section 6, Source Water Chemistry, are carried forward to this section for further evaluation.





**Figure 7-1.**

## 7.2. Develop Cycles-of-Concentration Scenarios

The speciated and balanced source water found in Table 6-4 will be used as a basis for all subsequent calculations. Enter the data (constituents as  $\text{mg/l}_{\text{specie}}$ ) from Table 6-4 into the “Source Water Data” column of Table 7-1, Concentration Scenarios. Five cycles-of-concentration scenarios—4, 6, 8, 10, and 12—will be evaluated.

### 7.2.1. Preliminary Cooling Tower Chemistry

Calculate concentrations for non-speciated constituents. These constituents include  $\text{Na}^{+1}$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Cl}^{-1}$ ,  $\text{NO}_3^{-1}$ ,  $\text{NO}_2^{-1}$ , and  $\text{SiO}_2$ . Ammonia, carbonate, and phosphate constituents will be speciated in subsequent sections. The sulfate concentration will be determined using data from alkalinity speciation, because it is assumed that sulfuric acid will be used to control cooling tower pH.

To calculate constituent concentrations, multiply the value for source water by the cycles of concentration and place the value in the appropriate column. For example, for sodium, multiply the source water value of  $122.7 \text{ mg/l}_{\text{Na}}$  by 4 to obtain the cooling tower concentration at 4 cycles ( $490.8 \text{ mg/l}_{\text{Na}}$ ). Continue this calculation for the remaining concentration scenarios for  $\text{Na}^{+1}$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Cl}^{-1}$ ,  $\text{NO}_3^{-1}$ ,  $\text{NO}_2^{-1}$ , and  $\text{SiO}_2$ , and insert the values into Table 7-1 (located after Figure 7-7).

### 7.2.2. Speciation

To start the speciation analysis, a preliminary cooling tower pH must be selected. For source waters that contain orthophosphate, such as those mentioned in Section 6, a pH of 7.0 will be assumed. Typically, cooling towers utilizing water with orthophosphates (e.g., treated municipal effluent) are operated within a pH range of 6.8 to 7.2. For source waters that do not contain orthophosphate, assume a preliminary pH of 8.0 (this is a commonly used alkaline pH). The spreadsheet calculator provided in Section 8 can be used to refine pH selection.

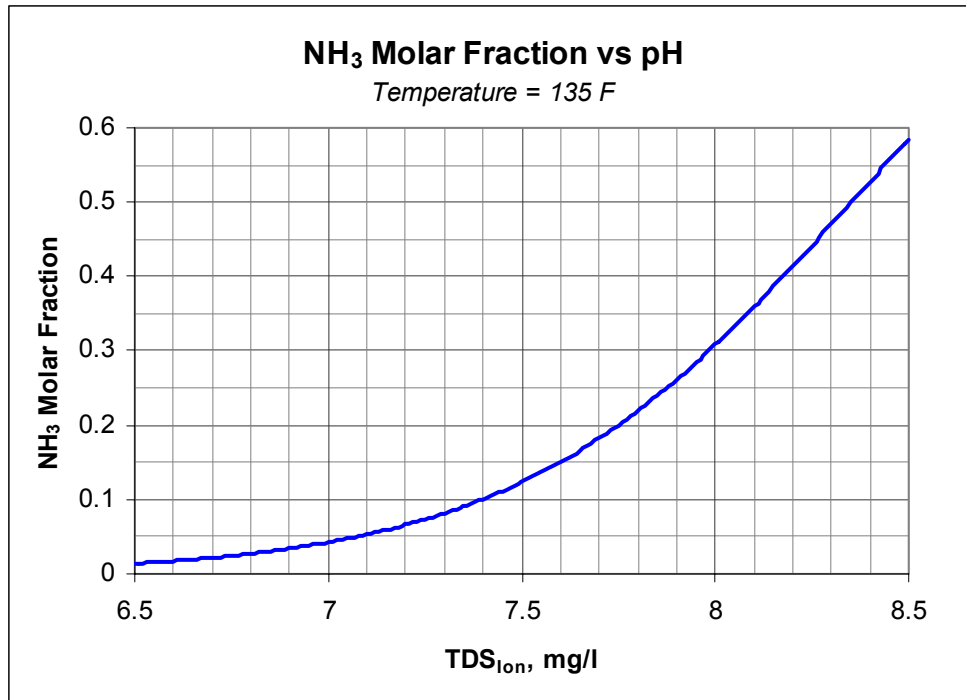
Lastly, the figures in this section used to predict molar fractions and the solubility of scale forming salts are based on a hot-side cooling water temperature of  $135^{\circ}\text{F}$  ( $57.2^{\circ}\text{C}$ ). This temperature, which conservatively represents a hottest-day-of-the-summer condition for a power plant condenser (even in desert settings), is used because most scale-forming compounds are less soluble at higher temperatures (except for silica).

### 7.2.3. Ammonia Speciation

Refer to the Figure 7-2 to obtain the ammonia ( $\text{NH}_3$ ) constituent speciation fraction (the smaller of the two component fractions in the pH range of interest). The  $\text{NH}_4^{+1}$  molar fraction can be calculated by difference, as described in Section 6. Enter the values in the ammonia worksheet.

Constituent fractions are different at higher temperatures than source water chemistry, which is assumed to be  $77^{\circ}\text{F}$  ( $25^{\circ}\text{C}$ ). For example, at a temperature of  $77^{\circ}\text{F}$  and a pH of 7.0, the  $\text{NH}_3$  fraction is 0.06. At  $135^{\circ}\text{F}$  ( $57.2^{\circ}\text{C}$ ) and a pH of 7.0, it is 0.04. Also recall that ionic strength does not effect ammonia molar fraction concentrations.

Transfer the total ammonia concentration in the source water from Table 6-4 to the worksheet (expressed as  $\text{mg/l}_\text{N}$ ). Next, apply the  $\text{NH}_4^{+1}$  and  $\text{NH}_3$  speciation fractions and reconvert to specie concentrations. These values will be used as the speciation basis for calculating cycled concentrations of  $\text{NH}_4^{+1}$  and  $\text{NH}_3$ . Multiply the basis values for  $\text{NH}_4^{+1}$  and  $\text{NH}_3$  by cycles of concentration (4, 6, 8, etc.) and enter the basis and cycled concentration values in the appropriate columns in Table 7-3.



**Figure 7-2.**

### Ammonia Calculation Worksheet

Preliminary Cooling Tower pH		7.0				
NH <sub>3</sub> Fraction (1)	A	0.04				
NH <sub>4</sub> <sup>+1</sup> Fraction (2)	B=1-A	0.96				
Total Ammonia, mg/l <sub>N</sub> (3)	C	18.0				
Basis NH <sub>3</sub> , mg/l <sub>NH3</sub>	D=1.21xAxC	0.87				
Basis NH <sub>4</sub> <sup>+1</sup> , mg/l <sub>NH4</sub>	E=1.29xBxC	22.3				
Cycles of Concentration	F	4	6	8	10	12
NH <sub>3</sub> , mg/l <sub>NH3</sub>	DxF	3.5	5.2	7.0	8.7	10.4
NH <sub>4</sub> <sup>+1</sup> , mg/l <sub>NH4</sub>	ExF	89.2	133.8	178.4	223.0	267.6

**Notes**

1. Obtained from Figure 7-1.
2. Calculated by difference.
3. Obtained from Table 6-4.

Worksheet concentrations for NH<sub>3</sub> and NH<sub>4</sub><sup>+</sup> are quite high, especially at higher cycles of concentration. It is likely that a significant amount of ammonia is lost to the air stream of the cooling tower. Some ammonia will react with halogen-based biocides to form chloramines and bromamines. To be conservative, this analysis does not take either loss mechanism into account.

#### 7.2.4. Alkalinity Speciation

Alkalinity will be established based on the preliminary pH selected for the cooling tower—in this case, a pH of 7.0 for the sample source water with orthophosphate present. For any given pH, most cooling towers will respond within a certain range of cooling water alkalinities. Factors that effect the alkalinity response of cooling towers include (some to a greater degree than others): ionic strength of circulating water, cooling-water- flow-to-air-stream-flow ratio (L/G ratio), packing type, proximity to combustion-exhaust plumes containing CO<sub>2</sub>, ambient temperature, and others. A number of alkalinity-pH relationships have been developed for cooling towers. Kunz et al. (1977) studied over 400 cooling systems and found significant variations in observed pH-to-alkalinity operating conditions. Later, Caplan (1990) refined the Kunz data using more-sophisticated data-analysis tools to produce the following relationship:

$$\log_{10}(M \text{ Alk}) = \frac{pH - 3.995}{1.794} \quad (30)$$

Where:  $M \text{ Alk}$       M Alkalinity, mg/l<sub>CaCO<sub>3</sub></sub>  
 $pH$               Cooling water pH

Caplan reviewed the work of a number of authors and surveyed a significant number of cooling tower operations to develop the relationship represented by Equation 30.

Using Equation 30, the M Alkalinity of the cooling tower is calculated to be 47 mg/l<sub>CaCO<sub>3</sub></sub>. Use the balanced and speciated TDS value found in Table 6-4 to calculate a preliminary cooling tower TDS based on the cycles-of-concentration scenarios. TDS will be refined later in this section of the report. Note that constituent molar fractions are not very sensitive to small changes in ionic strength. Refer to the Alkalinity Calculation Worksheet that follows.

Enter the speciation fractions for CO<sub>3</sub><sup>-2</sup> and CO<sub>2</sub> found in Figures 7-3 and 7-4. Next, calculate the calcium-carbonate equivalent concentrations for the alkalinity constituents. These values will be used next in this section to determine sulfuric acid requirements.

Finally, convert the calcium carbonate equivalent concentrations to specie concentrations by dividing by the conversion factors found in Table 6-1. Transfer the values for HCO<sub>3</sub><sup>-1</sup>, CO<sub>3</sub><sup>-2</sup>, and CO<sub>2</sub> to Table 7-1.

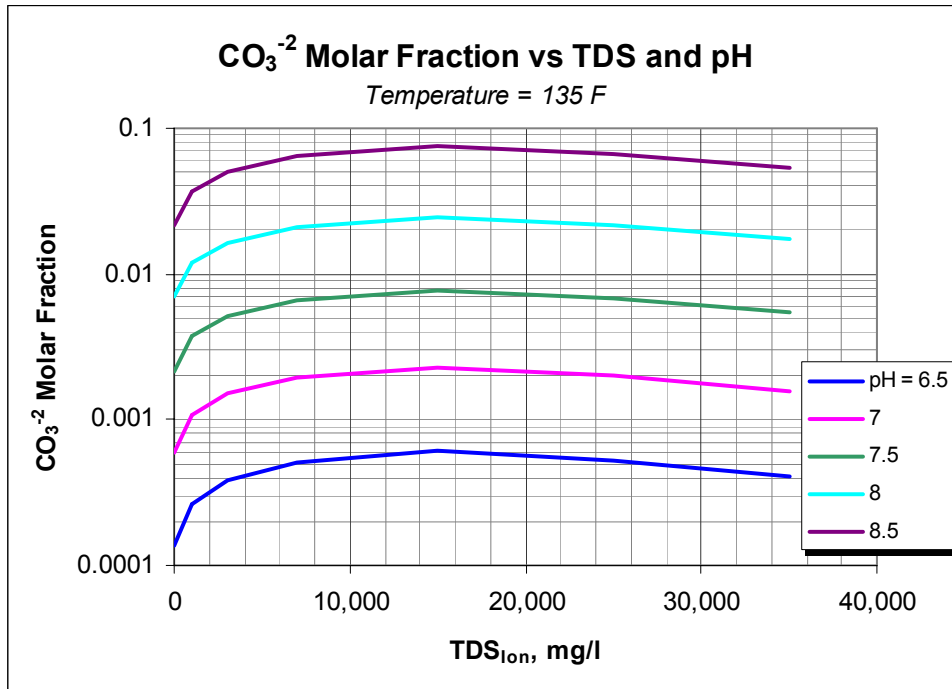


Figure 7-3.

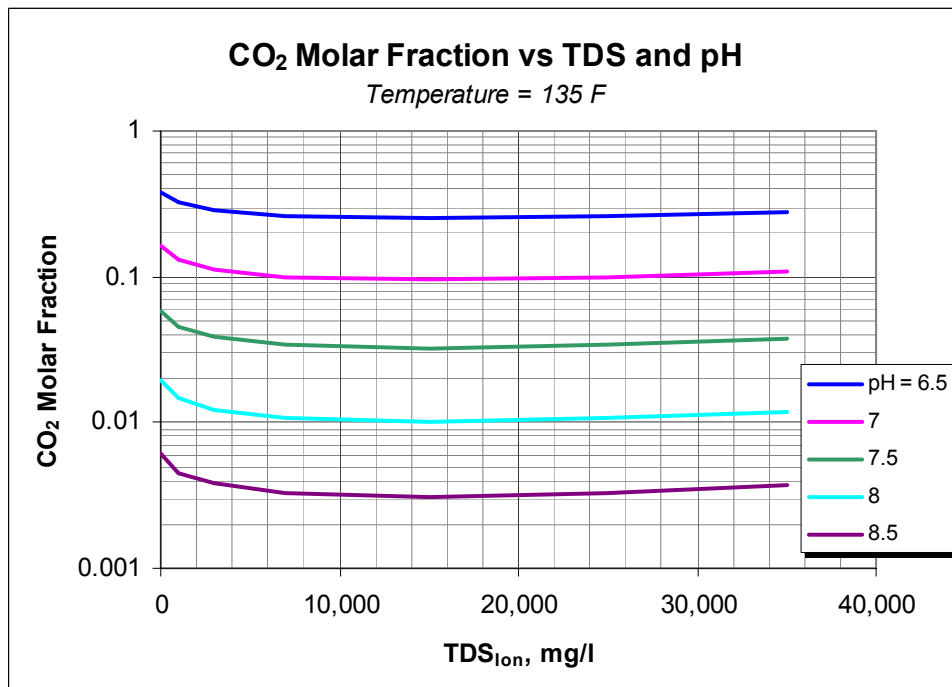


Figure 7-4.

### Alkalinity Calculation Worksheet

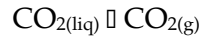
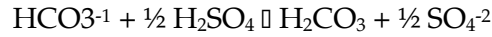
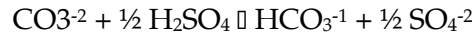
Preliminary Cooling Tower pH		7.0				
Calculated M Alkalinity, mg/l <sub>CaCO3</sub> (1)	A	47				
Source Water TDS, mg/l	B	707				
Cycles of Concentration	C	4	6	8	10	12
Prelim Cooling Tower TDS, mg/l (2)	CxD	2,828	4,242	5,656	7,070	8,484
CO <sub>3</sub> <sup>-2</sup> Fraction (3)	E	1.4x10 <sup>-3</sup>	1.5x10 <sup>-3</sup>	1.8x10 <sup>-3</sup>	2.0x10 <sup>-3</sup>	2.0x10 <sup>-3</sup>
CO <sub>2</sub> Fraction (4)	F	0.12	0.11	0.10	0.10	0.10
HCO <sub>3</sub> <sup>-1</sup> Fraction (5)	G=1-E-F	0.879	0.889	0.898	0.898	0.898
HCO <sub>3</sub> <sup>-1</sup> , mg/l <sub>CaCO3</sub> (6)	H=A×G	41.3	41.7	42.2	42.2	42.2
CO <sub>3</sub> <sup>-2</sup> , mg/l <sub>CaCO3</sub> (6)	J=A×E	0.066	0.071	0.085	0.094	0.094
CO <sub>2</sub> , mg/l <sub>CaCO3</sub>	K=A×F	5.64	7.05	8.46	9.40	9.40
HCO <sub>3</sub> <sup>-1</sup> , mg/l <sub>HCO3</sub>	Ge0.82	50.4	50.9	51.5	51.5	51.5
CO <sub>3</sub> <sup>-2</sup> , mg/l <sub>CO3</sub>	Je1.67	0.040	0.043	0.051	0.056	0.056
CO <sub>2</sub> , mg/l <sub>CO2</sub>	Ke1.14	4.95	6.18	7.42	8.24	8.24

#### **Notes**

1. Cooling tower M alkalinity calculated from Equation 30.
2. Cooling tower TDS will be refined later in this section.
3. Obtained from Figure 7-3.
4. Obtained from Figure 7-4.
5. HCO<sub>3</sub><sup>-1</sup> calculated by difference.
6. HCO<sub>3</sub><sup>-1</sup> and CO<sub>3</sub><sup>-2</sup> expressed as mg/l<sub>CaCO3</sub> will be used later to calculate sulfuric acid requirements and cooling tower sulfate concentration for each scenario.

### 7.2.5. Determining the Sulfate Concentration

It is assumed that sulfuric acid will be used to control cooling tower pH (essentially all cooling systems use sulfuric acid for pH adjustment). The following reactions occur when sulfuring acid is added to cooling tower circulating water to control pH:



Bicarbonate and carbonate alkalinity are converted to carbonic acid ( $\text{H}_2\text{CO}_3$ ). Carbonic acid dissociates to dissolved  $\text{CO}_{2(\text{liq})}$  and water (this reaction is somewhat reversible). Finally, the dissolved  $\text{CO}_{2(\text{liq})}$  volatilizes into the air stream—a reaction that is also reversible. Depending on ambient conditions and cooling tower chemistry, atmospheric  $\text{CO}_{2(\text{g})}$  can be absorbed by the circulating water. For each equivalent of sulfuric acid added to the cooling tower, one equivalent of alkalinity is reduced. Using this relationship, the following equations can be used to calculate the sulfuric acid required to achieve the M alkalinities predicted for each of the cycles-of-concentration scenarios (in Section 7.2.3) and the resulting sulfate concentration.

$$H_2SO_{4,SW} = M \text{ Alk}_{SW} - \frac{M \text{ Alk}_{CT}}{N} \quad (31)$$

Where:

- $H_2SO_{4,SW}$  = Sulfuric acid added to the source water, mg/l $_{\text{CaCO}_3}$
- $M \text{ Alk}_{SW}$  = M (total) alkalinity of the source water, mg/l $_{\text{CaCO}_3}$
- $M \text{ Alk}_{CT}$  = M (total) alkalinity of the cooling tower, mg/l $_{\text{CaCO}_3}$
- $N$  = Cycles of concentration of the cooling tower

$$SO_4^{-2}_{CT} = N \left( SO_4^{-2}_{SW} + H_2SO_{4,SW} \right) \div 1.04 \quad (32)$$

Where:

- $SO_4^{-2}_{CT}$  = Sulfate concentration of the cooling water, mg/l $_{\text{SO}_4}$
- $N$  = Cycles of concentration of the cooling tower
- $SO_4^{-2}_{SW}$  = Sulfate concentration of the source water, mg/l $_{\text{CaCO}_3}$
- $H_2SO_{4,SW}$  = Sulfuric acid added to the source water, mg/l $_{\text{CaCO}_3}$

The conversion factor (1.04) in Equation 32 is used to convert  $\text{SO}_4^{2-}$  as  $\text{mg/l}_{\text{CaCO}_3}$  to  $\text{mg/l}_{\text{SO}_4}$ . Refer to Table 6-1. Use the following Sulfate Calculation Worksheet to determine sulfuric acid requirements and the sulfate concentration for each cycle-of-concentration scenario. Transfer the cooling water sulfate data to Table 7-1.

### Sulfate Calculation Worksheet

Cycles of Concentration	A	4	6	8	10	12
Preliminary Cooling Tower pH	-----	7.0				
Source Water M Alkalinity, $\text{mg/l}_{\text{CaCO}_3}$ (1)	B	204				
Cooling Tower M Alkalinity, $\text{mg/l}_{\text{CaCO}_3}$ (2)	C	47				
Source Water $\text{SO}_4^{2-}$ , $\text{mg/l}_{\text{CaCO}_3}$ (1)	D	130				
$\text{H}_2\text{SO}_4$ added to Source Water, $\text{mg/l}_{\text{CaCO}_3}$ (3)	$E=B-C/A$	192.3	196.2	198.1	199.3	200.1
Cooling Tower $\text{SO}_4^{2-}$ , $\text{mg/l}_{\text{SO}_4}$ (4)	$A \times (D+E)/1.04$	1,239.6	1,881.9	2,523.8	3,166.3	3,808.8

#### Notes

1. Obtained from Table 6-4.
2. Calculated from Equation 30.
3. Calculated from Equation 31.
4. Calculated from Equation 32.

### 7.2.6. Phosphate Speciation

This section only applies to source waters containing orthophosphate (e.g., reclaimed municipal effluent). It is assumed that the pH of the cooling tower circulating water will be 7.0 (pH may be refined later in Section 8). Refer to the following worksheet for a determination of phosphate species.

Transfer the orthophosphate concentration of the source water from Table 6-4 (expressed as  $\text{mg/l}_P$ ) to the worksheet. Calculate the TDS of the circulating water for the different cycles-of-concentration scenarios. Obtain phosphate fractions— $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^{-1}$ , and  $\text{PO}_4^{-3}$ —from Figures 7-5, 7-6, and 7-7 for each concentration scenario.  $\text{HPO}_4^{-2}$  was calculated by difference for each concentration scenario. Lastly, calculate the concentrations for the phosphate constituents as  $\text{mg/l}_{\text{specie}}$ , as described in the worksheet. Enter the concentration values in Table 7-1.

### 7.2.7. Summarize the Cycles-of-Concentration Scenarios Data

Table 7-1 contains the results of all the calculations performed to this point in this section of the report. Calculate  $\text{TDS}_{\text{Ion}}$  by summing the ionic species (all species excluding  $\text{SiO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_3\text{PO}_4$ , and  $\text{CO}_2$ ).  $\text{TDS}_{\text{Ion}}$  is a gross measure of ionic strength and will be used to determine activity coefficients. Electroneutrality is mostly achieved in the cycles-of-concentration scenarios. Slight electroneutrality variations occur during the speciation of carbonate alkalinity, ammonia, and phosphate compounds.



### Phosphate Calculation Worksheet

Cooling Tower pH	7.0					
Source Water Orthophosphate, mg/l <sub>P</sub> (1)	A	1.9				
Source Water TDS, mg/l	B	707				
Cycles of Concentration	C	4	6	8	10	12
Prelim Cooling Tower TDS, mg/l (2)	BxC	2,828	4,242	5,656	7,070	8,484
H <sub>3</sub> PO <sub>4</sub> Fraction (3)	D	5.0x10 <sup>-6</sup>	4.5x10 <sup>-6</sup>	4.0x10 <sup>-6</sup>	3.6x10 <sup>-6</sup>	3.5x10 <sup>-6</sup>
H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup> Fraction (3)	E	0.30	0.28	0.25	0.23	0.22
PO <sub>4</sub> <sup>-3</sup> Fraction (3)	F	2.7x10 <sup>-5</sup>	3.0x10 <sup>-5</sup>	3.7x10 <sup>-5</sup>	4.3x10 <sup>-5</sup>	4.5x10 <sup>-5</sup>
HPO <sub>4</sub> <sup>-2</sup> Fraction (4)	G	0.70	0.72	0.75	0.77	0.78
H <sub>3</sub> PO <sub>4</sub> , mg/l <sub>H<sub>3</sub>PO<sub>4</sub></sub> (5)	3.16xAxCxD	1.2x10 <sup>-4</sup>	1.6x10 <sup>-4</sup>	1.9x10 <sup>-4</sup>	2.1x10 <sup>-4</sup>	2.5x10 <sup>-4</sup>
H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup> , mg/l <sub>H<sub>2</sub>PO<sub>4</sub></sub> (5)	3.13xAxCxE	7.13	10.0	11.9	13.7	15.7
HPO <sub>4</sub> <sup>-2</sup> , mg/l <sub>HPO<sub>4</sub></sub> (5)	3.10xAxCxG	16.5	25.4	35.3	45.4	55.1
PO <sub>4</sub> <sup>-3</sup> , mg/l <sub>PO<sub>4</sub></sub> (5)	3.06xAxCxF	6.3x10 <sup>-4</sup>	1.1x10 <sup>-3</sup>	1.7x10 <sup>-3</sup>	2.5x10 <sup>-3</sup>	3.1x10 <sup>-3</sup>

#### **Notes**

1. Obtained from Table 6-4.
2. Cooling tower TDS rounded to the nearest 1,000 mg/l.
3. Obtained from Figures 7-5, 7-6, and 7-7.
4. H<sub>2</sub>PO<sub>4</sub><sup>-1</sup> calculated by difference.
5. The constants (i.e., 3.13, 3.10, etc.) represents the ratio of the molecular weight of specie (i.e. H<sub>2</sub>PO<sub>4</sub><sup>-1</sup>, HPO<sub>4</sub><sup>-2</sup>, etc.) to the molecular weight of phosphorous, P.

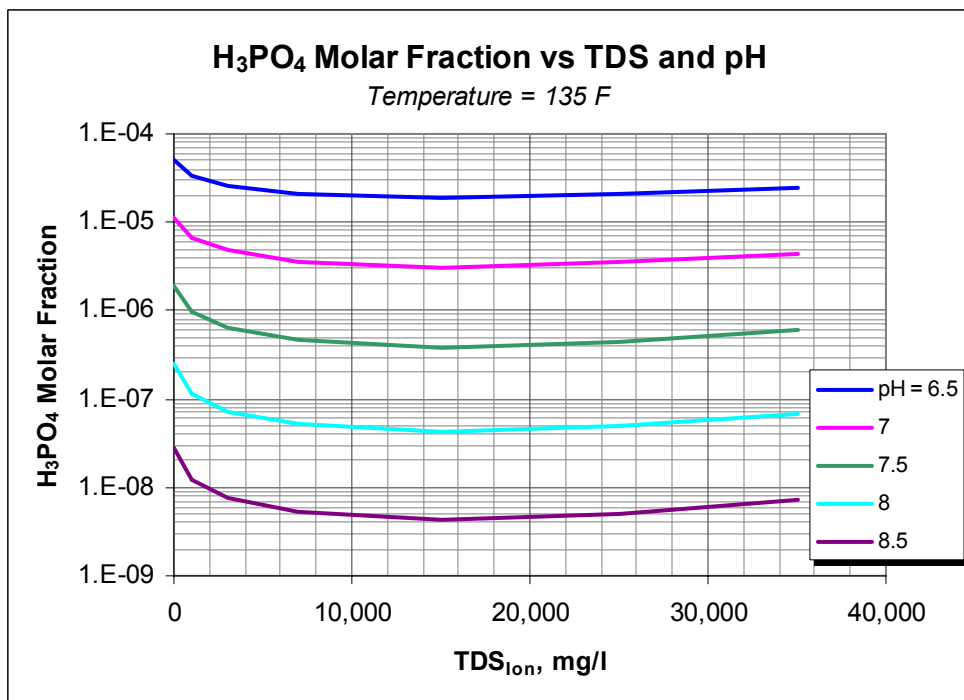


Figure 7-5.

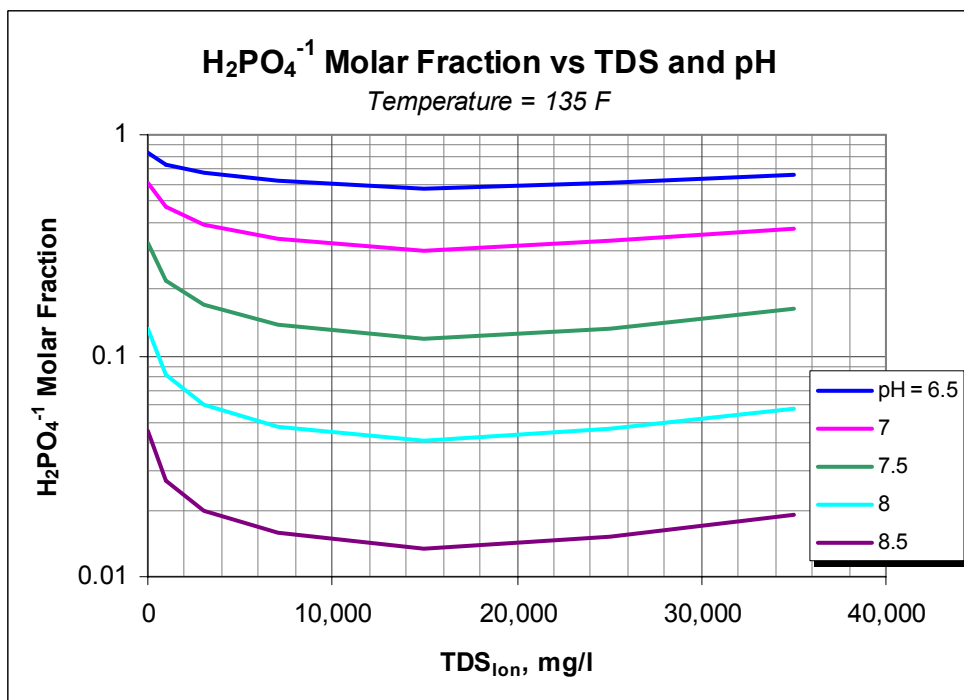
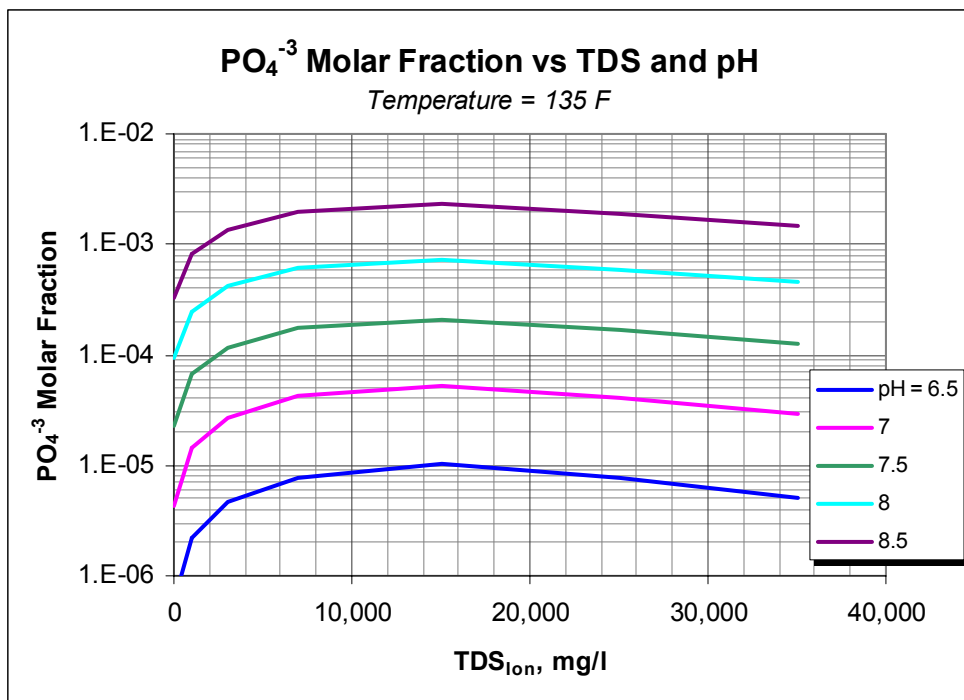


Figure 7-6.



**Figure 7-7.**

**Table 7-1. Cycle-of-Concentration Scenarios**

	Units	Source Water Data (1)	Cycles of Concentration				
			4	6	8	10	12
Na <sup>+1</sup>	mg/l <sub>Na</sub>	122.7	490.8	736.2	981.6	1,227.0	1,472.4
K <sup>+1</sup>	mg/l <sub>K</sub>	12.5	50.0	75.0	100.0	125.0	150.0
Ca <sup>+2</sup>	mg/l <sub>Ca</sub>	32.6	130.4	195.6	260.8	326.0	391.2
Mg <sup>+2</sup>	mg/l <sub>Mg</sub>	15.5	62.0	93.0	124.0	155.0	186.0
NH <sub>4</sub> <sup>+1</sup>	mg/l <sub>NH4</sub>	22.8	89.2	133.8	178.4	223.0	267.6
HCO <sub>3</sub> <sup>-1</sup>	mg/l <sub>HCO3</sub>	238.4	50.4	50.9	51.5	51.5	51.5
CO <sub>3</sub> <sup>-2</sup>	mg/l <sub>CO3</sub>	0.24	0.040	0.043	0.051	0.056	0.056
Cl <sup>-1</sup>	mg/l <sub>Cl</sub>	107.7	430.8	646.2	861.6	1,077.0	1,292.4
SO <sub>4</sub> <sup>-2</sup>	mg/l <sub>SO4</sub>	125	1,239.6	1,881.9	2,523.8	3,166.3	3,808.8
NO <sub>3</sub> <sup>-1</sup>	mg/l <sub>NO3</sub>	3.1	12.4	18.6	24.8	31.0	37.2
NO <sub>2</sub> <sup>-1</sup>	mg/l <sub>NO2</sub>	4.6	18.4	27.7	36.9	46.1	55.3
H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup>	mg/l <sub>H2PO4</sub>	1.5	7.13	10.0	11.9	13.7	15.7
HPO <sub>4</sub> <sup>-2</sup>	mg/l <sub>HPO4</sub>	4.4	16.5	25.4	35.3	45.4	55.1
PO <sub>4</sub> <sup>-3</sup>	mg/l <sub>PO4</sub>	7.5x10 <sup>-5</sup>	0.00063	0.0011	0.0017	0.0025	0.0031
TDS <sub>Ion</sub> (2)	mg/l	691	2,593	3,886	5,181	6,475	7,769
SiO <sub>2</sub>	mg/l <sub>SiO2</sub>	16	64	96	128	160	192
NH <sub>3</sub>	mg/l <sub>NH3</sub>	0.36	3.5	5.2	7.0	8.7	10.4
H <sub>3</sub> PO <sub>4</sub>	mg/l <sub>H3PO4</sub>	6.0x10 <sup>-6</sup>	1.2x10 <sup>-4</sup>	1.6x10 <sup>-4</sup>	1.9x10 <sup>-4</sup>	2.1x10 <sup>-4</sup>	2.5x10 <sup>-4</sup>
CO <sub>2</sub>	mg/l <sub>CO2</sub>	7.2	4.95	6.18	7.42	8.24	8.24
TDS (3)	mg/l	707	2,657	3,982	5,309	6,635	7,961
pH	----	7.5	7.0	7.0	7.0	7.0	7.0
M Alkalinity, mg/l <sub>CaCO3</sub> (4)			47	47	47	47	47
Sulfuric Acid, H <sub>2</sub> SO <sub>4</sub> , mg/l <sub>CaCO3</sub>			192.3	196.2	198.1	199.3	200.1

**Notes:**

Re-specified data values based on cooling tower control pH.

1. Speciated and balanced source water data from Table 6-4.
2. Sum of ion concentrations (does not include SiO<sub>2</sub>, NH<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, and CO<sub>2</sub>).
3. Sum of all ionic and soluble constituents except volatiles (CO<sub>2</sub> and NH<sub>3</sub>).
4. Obtained from Table 6-4.

### 7.3. Ion Association and Ion Activity

Cooling tower circulating water can have relatively high levels of sulfate ions as a result of source water concentrations and sulfuric acid addition. The source water example used thus far in the analysis generated sulfate levels ranging from 1,239 mg/l to 3,808 mg/l at 4 to 12 cycles of concentration (refer to Table 7-1). Sulfate ions readily associate with calcium and magnesium ions, especially when compared to other association relationships. Focus is placed on calcium and magnesium, because they generate a number of scale-forming compounds. Other calcium and magnesium associations also occur (e.g.,  $\text{CaOH}^{+1}$ ,  $\text{CaCO}_3^0$ ,  $\text{MgOH}^{+1}$ ) but their concentrations are relatively minor (up to several orders of magnitude smaller) compared to the predominance of sulfate associations. Lastly, sodium, potassium, and ammonium associations also form, but in concentrations that are proportionately insignificant.

In this section, calcium sulfate and magnesium sulfate ion associations are determined. Once these are established, activity coefficients for scale-forming cations and anions will be calculated, and the relative solubility of scale-forming compounds of concern will be determined.

#### 7.3.1. Calcium and Magnesium Sulfate Ion Association Analysis

A hot water return temperature of 135°F (57.2°C) will be assumed for subsequent ion association and solubility calculations. This temperature is equivalent to “hot day” operation for many inland cooling towers, and thus, constitutes a worst-case scenario for many scaling species. With the exception of  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 8\text{H}_2\text{O}$  and silica ( $\text{SiO}_2$ ), the compounds of scale to be discussed in this section are less soluble at higher temperatures.

The following derivation was used to calculate the degree of calcium sulfate and magnesium sulfate association.

$$[\text{SO}_4]_{\text{Total}} = [\text{SO}_4^{-2}]_{\text{Free}} + [\text{CaSO}_4^0] + [\text{MgSO}_4^0] \quad (30)$$

$$[\text{Ca}]_{\text{Total}} = [\text{Ca}^{+2}]_{\text{Free}} + [\text{CaSO}_4^0] \quad (31)$$

$$[\text{Mg}]_{\text{Total}} = [\text{Mg}^{+2}]_{\text{Free}} + [\text{MgSO}_4^0] \quad (32)$$

Where:	$[\text{SO}_4]_{\text{Total}}$	= Total molar concentration of $\text{SO}_4$ species
	$[\text{Ca}]_{\text{Total}}$	= Total molar concentration of Ca species
	$[\text{Mg}]_{\text{Total}}$	= Total molar concentration of Mg species
	$[\text{SO}_4^{-2}]_{\text{Free}}$	= Molar concentration of ionic $\text{SO}_4^{-2}$
	$[\text{Ca}^{+2}]_{\text{Free}}$	= Molar concentration of ionic $\text{Ca}^{+2}$
	$[\text{Mg}^{+2}]_{\text{Free}}$	= Molar concentration of ionic $\text{Mg}^{+2}$
	$[\text{CaSO}_4^0]$	= Molar concentration of $\text{CaSO}_4^0$ association
	$[\text{MgSO}_4^0]$	= Molar concentration of $\text{MgSO}_4^0$ association

The  $\text{CaSO}_4^0$  formation relationship follows:

$$K'_{F,\text{CaSO}_4^0} = \frac{[\text{CaSO}_4^0]}{[\text{Ca}^{+2}]_{\text{Free}}[\text{SO}_4^{-2}]_{\text{Free}}} \quad (33)$$

$K'_{F,\text{CaSO}_4}$  is the adjusted formation constant for calcium sulfate association. The constant was adjusted as follows:

$$K'_{F,\text{CaSO}_4^0} = K_{F,\text{CaSO}_4^0} \gamma_{\pm 2}^2 \quad (34)$$

Where  $\gamma_{\pm 2}$  is the activity coefficient for  $\text{Ca}^{+2}$  and  $\text{SO}_4^{-2}$ .

Rearranging Equation 33 yields:

$$[\text{CaSO}_4^0] = [\text{Ca}^{+2}]_{\text{Free}} [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{CaSO}_4^0} \quad (35)$$

Inserting Equation 35 into 31 yields:

$$[\text{Ca}]_{\text{Total}} = [\text{Ca}^{+2}]_{\text{Free}} + [\text{Ca}^{+2}]_{\text{Free}} [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{CaSO}_4^0} \quad (36)$$

Rearranging and solving for  $[\text{Ca}^{+2}]_{\text{Free}}$

$$[\text{Ca}^{+2}]_{\text{Free}} = \frac{[\text{Ca}]_{\text{Total}}}{1 + [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{CaSO}_4^0}} \quad (37)$$

Inserting Equation 37 into 35 yields:

$$[\text{CaSO}_4^0] = \frac{[\text{Ca}]_{\text{Total}} [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{CaSO}_4^0}}{1 + [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{CaSO}_4^0}} \quad (38)$$

Performing the same derivation for associated  $\text{MgSO}_4^0$  yields:

$$[\text{MgSO}_4^0] = \frac{[\text{Mg}]_{\text{Total}} [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{MgSO}_4^0}}{1 + [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{MgSO}_4^0}} \quad (39)$$

Inserting Equations 38 and 39 into Equation 30 yields:

$$[\text{SO}_4]_{\text{Total}} = [\text{SO}_4^{-2}]_{\text{Free}} + \frac{[\text{Ca}]_{\text{Total}} [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{CaSO}_4^0}}{1 + [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{CaSO}_4^0}} + \frac{[\text{Mg}]_{\text{Total}} [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{MgSO}_4^0}}{1 + [\text{SO}_4^{-2}]_{\text{Free}} K'_{F,\text{MgSO}_4^0}} \quad (40)$$

The formations constants for  $\text{CaSO}_4^0$  and  $\text{MgSO}_4^0$  are approximately equal at a circulating water temperature of 135 F.

$$K'_F = K'_{F,\text{CaSO}_4^0} \approx K'_{F,\text{MgSO}_4^0} \quad (41)$$

Equation 40 simplifies to the following:

$$[SO_4]_{Total} = [SO_4^{-2}]_{Free} + \left\{ \frac{[SO_4^{-2}]_{Free} K'_F}{1 + [SO_4^{-2}]_{Free} K'_F} \right\} ([Ca]_{Total} + [Mg]_{Total}) \quad (42)$$

Rearranging Equation 42 yields the following quadratic expression:

$$K'_F [SO_4^{-2}]_{Free}^2 + (1 + ([Ca]_{Total} + [Mg]_{Total} - [SO_4]_{Total}) K'_F) [SO_4^{-2}]_{Free} - [SO_4]_{Total} = 0 \quad (43)$$

Simplifying Equation 43 yields:

$$a[SO_4^{-2}]_{Free}^2 + b[SO_4^{-2}]_{Free} + c = 0 \quad (44)$$

$$\text{Where: } a = K'_F \quad (45)$$

$$b = 1 + ([Ca]_{Total} + [Mg]_{Total} - [SO_4]_{Total}) K'_F \quad (46)$$

$$c = -[SO_4]_{Total} \quad (47)$$

Solving for  $[SO_4^{-2}]_{Free}$  yields the following quadratic solution:

$$[SO_4^{-2}]_{Free} = \frac{-b + \sqrt{b^2 - 4ac}}{2a} \quad (48)$$

The quadratic solution for Equation 44 requires the “ $-b \pm (b^2 - 4ac)^{1/2}$ ” term to be “ $-b + (b^2 - 4ac)^{1/2}$ ” to yield a realistic answer. Refer to Figures 7-8 (broad range of calcium and magnesium to sulfate ratios) and 7-9 (low range) for derived calcium sulfate and magnesium sulfate formation. The analysis used to develop Figures 7-8 and 7-9, in addition to using the  $[SO_4^{-2}]_{Free}$  derivation, included a determination of source water chemistry by establishing a cooling tower alkalinity of 100 mg/l<sub>CaCO3</sub> and balancing the chemistry to “zero” electroneutrality to determine a resultant sodium or chloride concentration. After the chemistry was determined, ionic strength was calculated and the formation constant was adjusted. The results compared favorably to an analysis by the calculator in Section 8.

### 7.3.2. Ion Association

The compounds  $CaSO_4^0$  and  $MgSO_4^0$  are estimated using the simplified ion association analysis derived above. Refer to Figures 7-8 and 7-9. Transfer  $Ca^{+2}$ ,  $Mg^{+2}$ ,  $SO_4^{-2}$ , and  $TDS_{Ion}$  data from Table 7-1 into the Ion Association Worksheet. The concentrations of  $Ca^{+2}$ ,  $Mg^{+2}$  and  $SO_4^{-2}$  are converted from mg/l<sub>specie</sub> to mg/l<sub>CaCO3</sub> and calculate the ratio of  $Ca^{+2}$  plus  $Mg^{+2}$  to  $SO_4^{-2}$ . Using the  $TDS_{Ion}$  of the cycled water for each cycles-of-concentration scenario and the  $Ca^{+2}$ -plus- $Mg^{+2}$ -to- $SO_4^{-2}$  ratio, determine the free  $SO_4^{-2}$  fraction of total  $SO_4$  species. Refer to Figure 7-8 or 7-9.

Next,  $CaSO_4$  and  $MgSO_4$  ion associations and free  $Ca^{+2}$  and  $Mg^{+2}$  are calculated—all expressed as mg/l<sub>CaCO3</sub>. Recall that the formation constants for  $CaSO_4^0$  and  $MgSO_4^0$  are approximately the same at 135°F (57.2°C); therefore,  $CaSO_4^0$  and  $MgSO_4^0$  are calculated using a proportioning relationship. Reconvert the  $Ca^{+2}$ ,  $Mg^{+2}$ , and  $SO_4^{-2}$  to mg/l<sub>specie</sub> and recalculate  $TDS_{Ion}$ . Transfer these values to the Ion Activity Worksheet where this data will be used to calculate activity concentrations of scale-forming compounds.

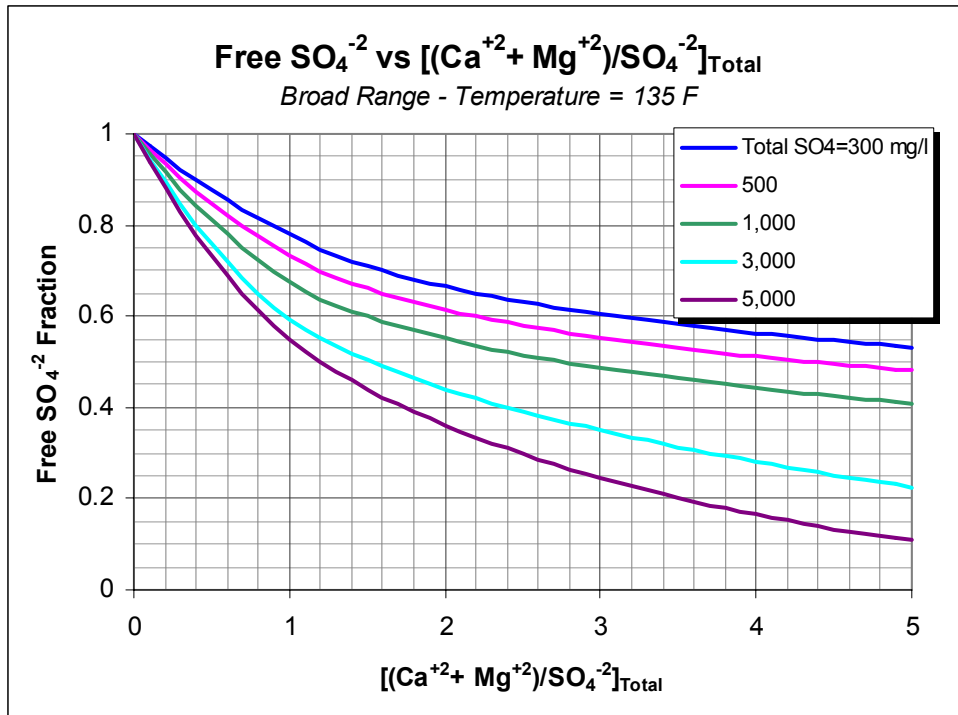


Figure 7-8.

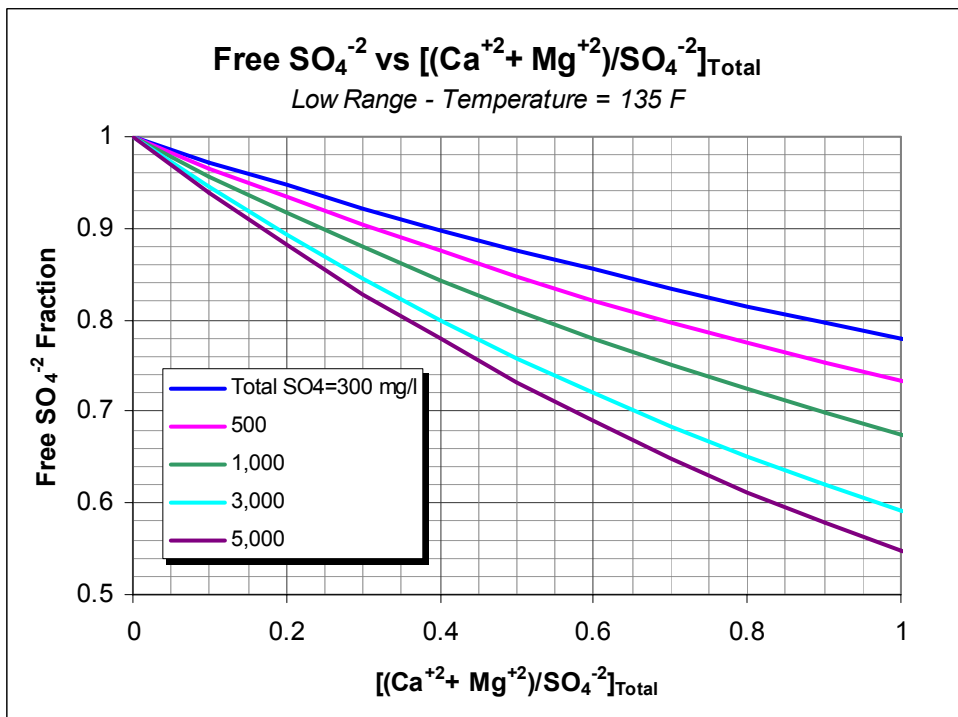


Figure 7-9.



## Ion Association Worksheet

		Units	Cycles of Concentration				
			4	6	8	10	12
Total Ca (1)	A	mg/l <sub>Ca</sub>	130.4	195.6	260.8	326.0	391.2
Total Mg (1)	B	mg/l <sub>Mg</sub>	62.0	93.0	124.0	155.0	186.0
Total SO <sub>4</sub> (1)	C	mg/l <sub>SO4</sub>	1,239.6	1,881.9	2,523.8	3,166.3	3,808.8
TDS <sub>Ion</sub> (1)	Q	mg/l	2,593	3,886	5,181	6,475	7,769
Total Ca (2)	D=2.50Xa	mg/l <sub>CaCO3</sub>	326.0	489.0	652.0	815.0	978.0
Total Mg (2)	E=4.12xB	mg/l <sub>CaCO3</sub>	255.4	383.2	510.9	638.6	766.3
Total SO <sub>4</sub> (2)	F=1.04xC	mg/l <sub>CaCO3</sub>	1,289.2	1,957.2	2,624.8	3,293.0	3,961.2
(Ca+Mg)/SO <sub>4</sub> Ratio	(D+E)/F	mg/l <sub>CaCO3</sub>	0.45	0.45	0.44	0.44	0.44
Free SO <sub>4</sub> <sup>-2</sup> Fraction (3)	G	-----	0.82	0.80	0.79	0.78	0.77
Assoc SO <sub>4</sub> Fraction	H=1-G	-----	0.18	0.20	0.21	0.22	0.23
CaSO <sub>4</sub> <sup>0</sup> + MgSO <sub>4</sub> <sup>0</sup>	J=FxH	mg/l <sub>CaCO3</sub>	232.1	391.4	551.2	724.5	911.1
CaSO <sub>4</sub> <sup>0</sup>	K=JxD/(D+E)	mg/l <sub>CaCO3</sub>	130.1	219.6	309.2	406.4	511.1
MgSO <sub>4</sub> <sup>0</sup>	L=J-K	mg/l <sub>CaCO3</sub>	102.0	171.8	242.0	318.1	400.0
Free Ca <sup>+2</sup>	M=D-K	mg/l <sub>CaCO3</sub>	195.9	269.4	342.8	408.6	466.9
Free Mg <sup>+2</sup>	N=E-L	mg/l <sub>CaCO3</sub>	153.4	211.4	268.9	320.5	366.3
Free SO <sub>4</sub> <sup>-2</sup>	P=F-J	mg/l <sub>CaCO3</sub>	1,057.1	1,565.8	2,073.6	2,568.5	3,050.1
Free Ca <sup>+2</sup> (2)	R=M/2.50	mg/l <sub>Ca</sub>	78.4	107.8	137.1	163.4	186.8
Free Mg <sup>+2</sup> (2)	S=N/4.12	mg/l <sub>Mg</sub>	37.2	51.3	65.3	77.8	88.9
Free SO <sub>4</sub> <sup>-2</sup> (2)	T=P/1.04	mg/l <sub>SO4</sub>	1,016.4	1,505.6	1,993.8	2,469.7	2,933.8
Adjusted TDS <sub>Ion</sub>	U=Q-(A-R)-(B-S)-(C-T)	mg/l	2,293	3,380	4,469	5,539	6,593

### Notes

1. Obtained from Table 7-1.
2. Refer to Table 6-1 for factors to convert species from mg/l<sub>Species</sub> to mg/l<sub>CaCO3</sub>.
3. Refer to Figures 7-8 and 7-9 to obtain free SO<sub>4</sub><sup>-2</sup> fraction.

### 7.3.3. Ion Activity

In this section, ion activities will be calculated for  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{OH}^{-1}$ ,  $\text{CO}_3^{-2}$ ,  $\text{SO}_4^{-2}$ , and  $\text{PO}_4^{-3}$ . Transfer values for free  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{SO}_4^{-2}$ , and  $\text{TDS}_{\text{Ion}}$  from the Ion Association Worksheet to the Ion Activity Worksheet below. Transfer values for  $\text{CO}_3^{-2}$  and  $\text{PO}_4^{-3}$  from Table 7-1. The concentration of  $\text{OH}^{-1}$  will be calculated.

Determine the  $\text{OH}^{-1}$  concentration as  $\text{mg}/\text{l}_{\text{Specie}}$  by referring to Figures 7-10 and 7-11. Each provides an  $\text{OH}^{-1}$  concentration for a pH range of 6.5 to 7.5 and 7.5 to 8.5, respectively. Locate the  $\text{OH}^{-1}$  concentration for a pH of 7.0 and the  $\text{TDS}_{\text{Ion}}$  associated with each cycles-of-concentration scenario. Enter the values into the Ion Activity worksheet.

Using  $\text{TDS}_{\text{Ion}}$  for each cycles-of-concentration scenario, determine the activity coefficients ( $\gamma_{\pm n}$ ) for  $\pm 1$ ,  $\pm 2$ , and  $\pm 3$  valence ions from Figure 7-12. Figure 7-12 is a modified version of Figure 3-2 (Activity Coefficient vs  $\text{TDS}_{\text{Ion}}$ ), found in Section 3.3, Ion Association. Figure 7-12 is a simplified version of the data, where only the uppermost values of the activity coefficients (i.e., the “top of the envelope”) are utilized to eliminate the relatively minor data scatter. These slightly higher values are also more conservative.

Convert the ion concentrations to ion activities, as instructed in the worksheet. Transfer the activity concentrations to Table 7-2. This data will be used to determine the relative solubility of scale-forming compounds in Section 7.3.4.

## Ion Activity Worksheet

		Units	Cycles of Concentration				
			4	6	8	10	12
Free Ca <sup>+2</sup> (1)	A	mg/l <sub>Ca</sub>	78.4	107.8	137.1	163.4	186.8
Free Mg <sup>+2</sup> (1)	B	mg/l <sub>Mg</sub>	37.2	51.3	65.3	77.8	88.9
OH <sup>-1</sup> (3)	C	mg/l <sub>OH</sub>	0.014	0.014	0.014	0.014	0.014
CO <sub>3</sub> <sup>-2</sup> (2)	D	mg/l <sub>CO3</sub>	0.040	0.043	0.051	0.056	0.056
Free SO <sub>4</sub> <sup>-2</sup> (1)	E	mg/l <sub>SO4</sub>	1,016.4	1,505.6	1,993.8	2,469.7	2,933.8
HPO <sub>4</sub> <sup>-2</sup> (2)	F	mg/l <sub>HPO4</sub>	16.5	25.4	35.3	45.4	55.1
PO <sub>4</sub> <sup>-3</sup> (2)	G	mg/l <sub>PO4</sub>	0.00063	0.0011	0.0017	0.0025	0.0031
Adjusted TDS <sub>Ion</sub> (1)		mg/l	2,293	3,380	4,469	5,539	6,593
pH (2)		----	7.0	7.0	7.0	7.0	7.0
γ <sub>±1</sub> (4)	H	----	0.82	0.80	0.77	0.76	0.75
γ <sub>±2</sub> (4)	J	----	0.44	0.40	0.37	0.34	0.33
γ <sub>±3</sub> (4)	K	----	0.17	0.13	0.11	0.09	0.08

### Calculate Activity Concentrations

$A_{\text{Ca}^{+2}}$	M=AxJ	mg/l <sub>Ca</sub>	34.5	43.1	50.7	55.6	61.6
$A_{\text{Mg}^{+2}}$	N=BxJ	mg/l <sub>Mg</sub>	16.4	20.5	24.2	26.4	29.3
$A_{\text{OH}^{-1}}$	N=CxH	mg/l <sub>OH</sub>	0.011	0.011	0.011	0.011	0.011
$A_{\text{CO}_3^{-2}}$	P=DxJ	mg/l <sub>CO3</sub>	0.018	0.017	0.019	0.019	0.018
$A_{\text{SO}_4^{-2}}$	Q=ExJ	mg/l <sub>SO4</sub>	447.2	602.2	737.7	839.7	968.2
$A_{\text{HPO}_4^{-2}}$	R=FxJ	mg/l <sub>HPO4</sub>	7.26	10.2	13.1	15.4	18.2
$A_{\text{PO}_3^{-3}}$	S=GxK	mg/l <sub>PO4</sub>	0.00011	0.00014	0.00019	0.00023	0.00025

### Notes

1. Obtained from the Ion Association Worksheet.
2. Obtained from Table 7-1.
3. Obtained from Figure 7-10 or 7-11.
4. Activity coefficients ( $\gamma_{\pm n}$ ) for valence  $\pm 1$ ,  $\pm 2$ , and  $\pm 3$  were obtained from Figure 7-12.

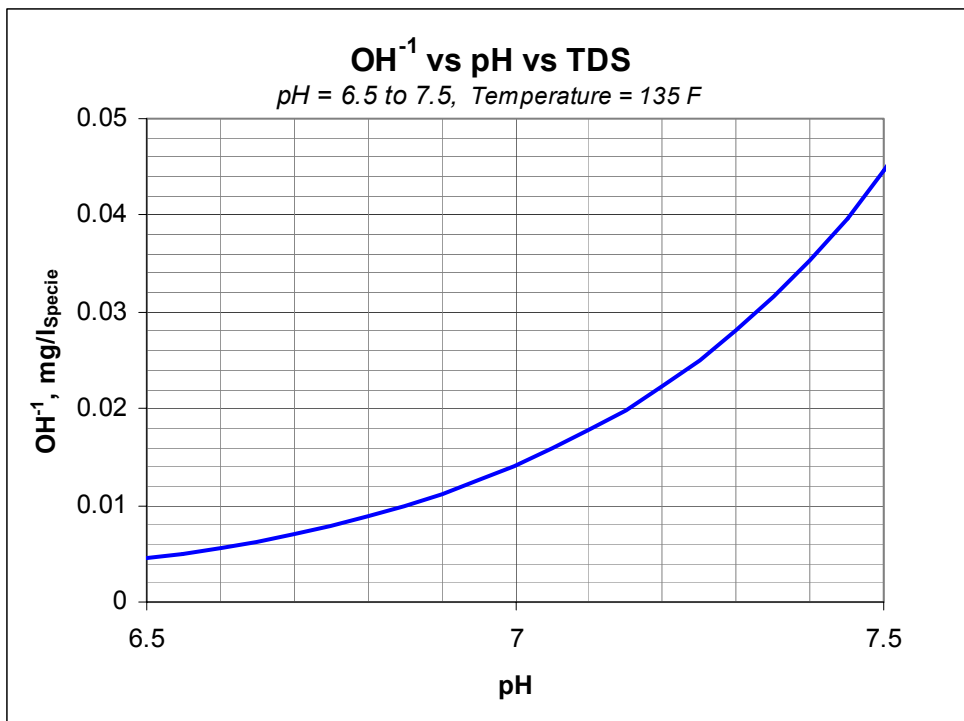


Figure 7-10.

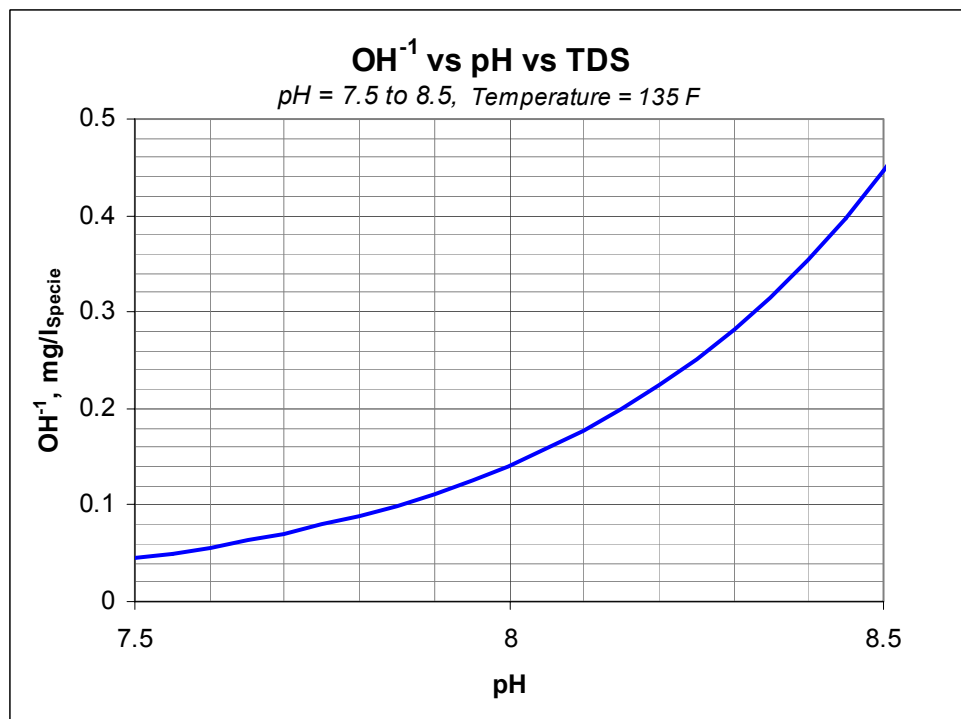


Figure 7-11.

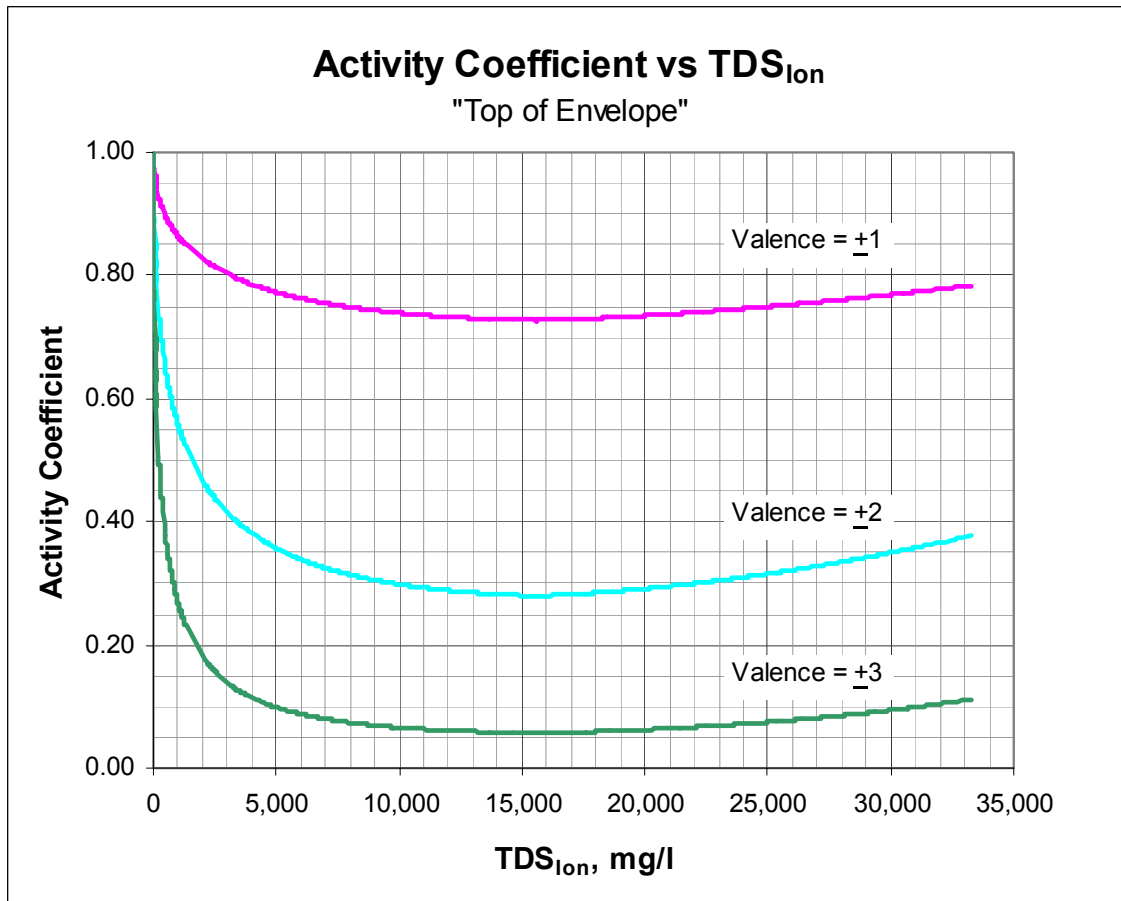


Figure 7-12.

#### 7.3.4. Relative Solubility of Scale-Forming Compounds

In this section, the relative saturation of scale-forming compounds will be determined. Relative saturation is defined as the product of the ion activities in solution to the theoretical solubility product. For example, the relative solubility for  $\text{CaCO}_3$  would be calculated as follows:

$$RS_{\text{CaCO}_3} = \frac{\text{Activity}_{\text{Ca}^{+2}} \text{Activity}_{\text{CO}_3^{-2}}}{K_{SP, \text{CaCO}_3}} \quad (49)$$

Where:  $K_{SP, \text{CaCO}_3}$  Solubility product for  $\text{CaCO}_3$

A relative solubility of greater than one would indicate that the salt is above saturation and products of scale will form. Less than one indicates that the salt has not reached saturation and scale will not form. A relative saturation of one indicates that the salt is at saturation.

The relative saturation of following scale-forming compounds will be determined:

Scale-Forming Compound	Common Name	Formula
Calcium Carbonate	Calcite, Aragonite	$\text{CaCO}_3$
Calcium Sulfate	Anhydrite	$\text{CaSO}_4$
Calcium Sulfate	Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Calcium Hydrogen Phosphate	Dicalcium phosphate, monetite	$\text{CaHPO}_4$
Calcium Phosphate	Tricalcium Phosphate	$\text{Ca}_3(\text{PO}_4)_2$
Magnesium Silicate	Sepiolite	$\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 8\text{H}_2\text{O}$
Silica		$\text{SiO}_2$

The solubility constants for  $\text{CaCO}_3$ ,  $\text{CaSO}_4$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ca}_3(\text{PO}_4)_2$ ,  $\text{CaHPO}_4$ , and  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$  can be found in Figures 7-13 to 7-17. With the exception of  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$ , solubility decreases as temperature increases.

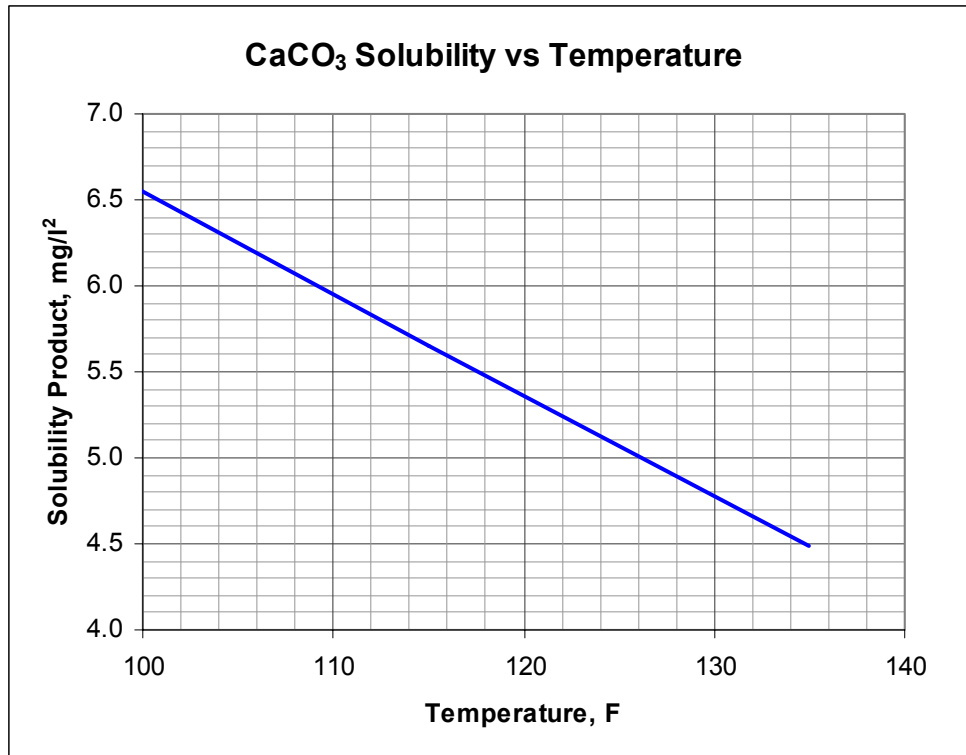


Figure 7-13.

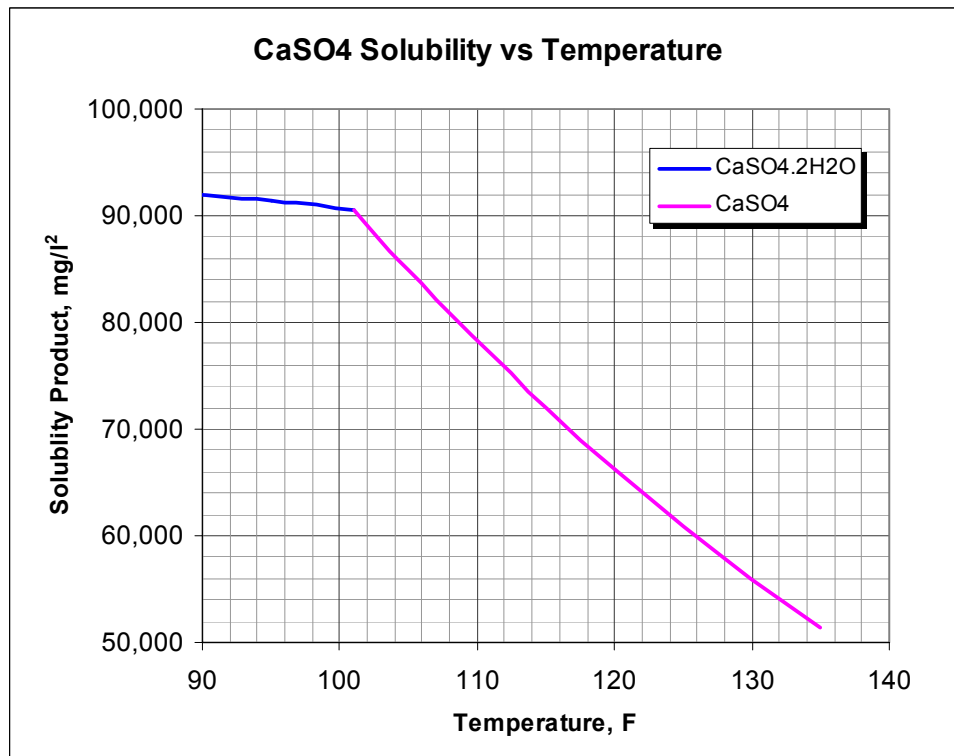


Figure 7-14.

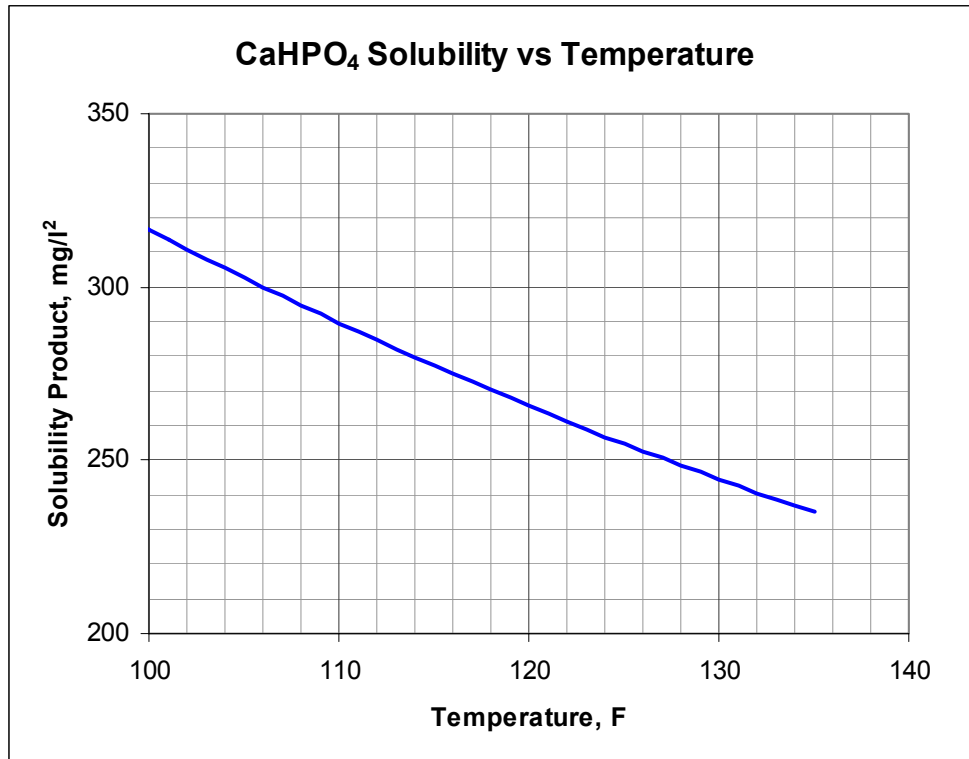


Figure 7-15.

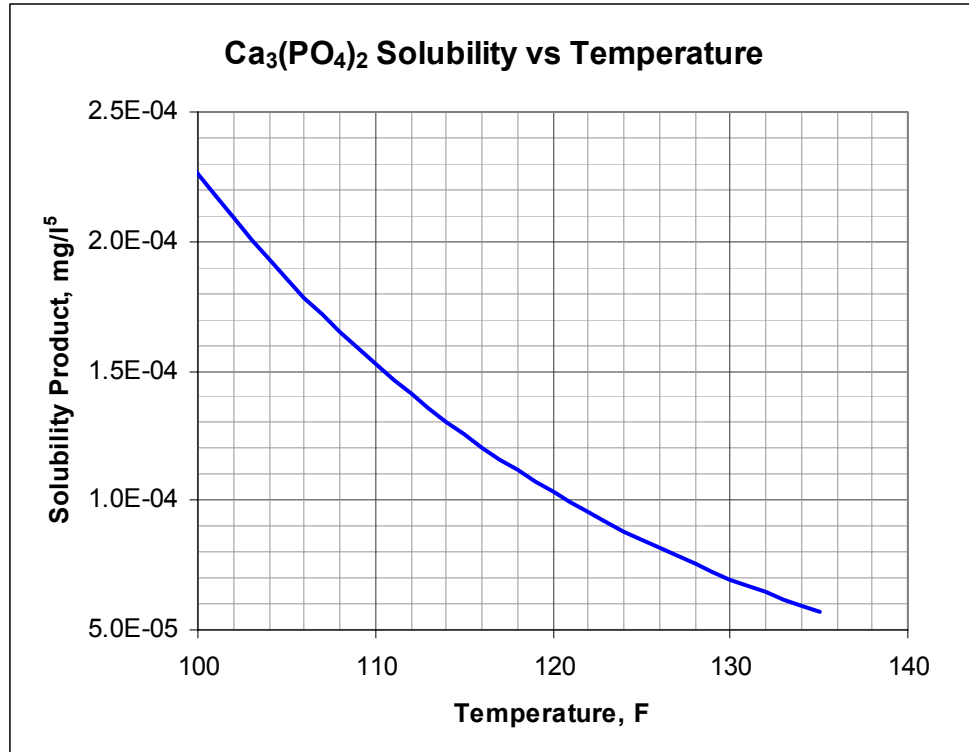
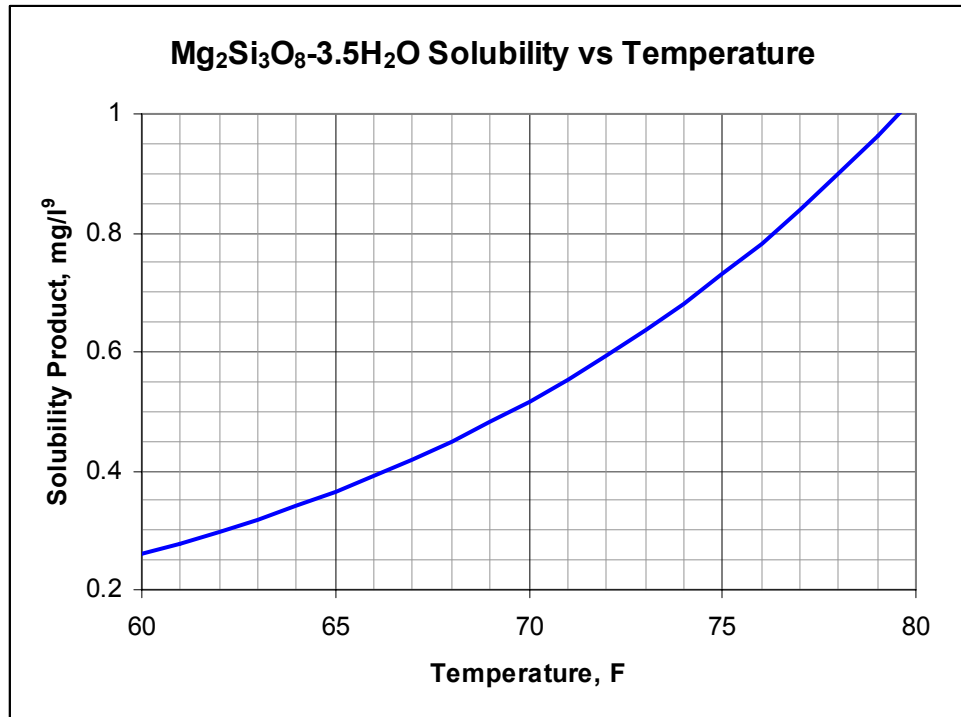


Figure 7-16.



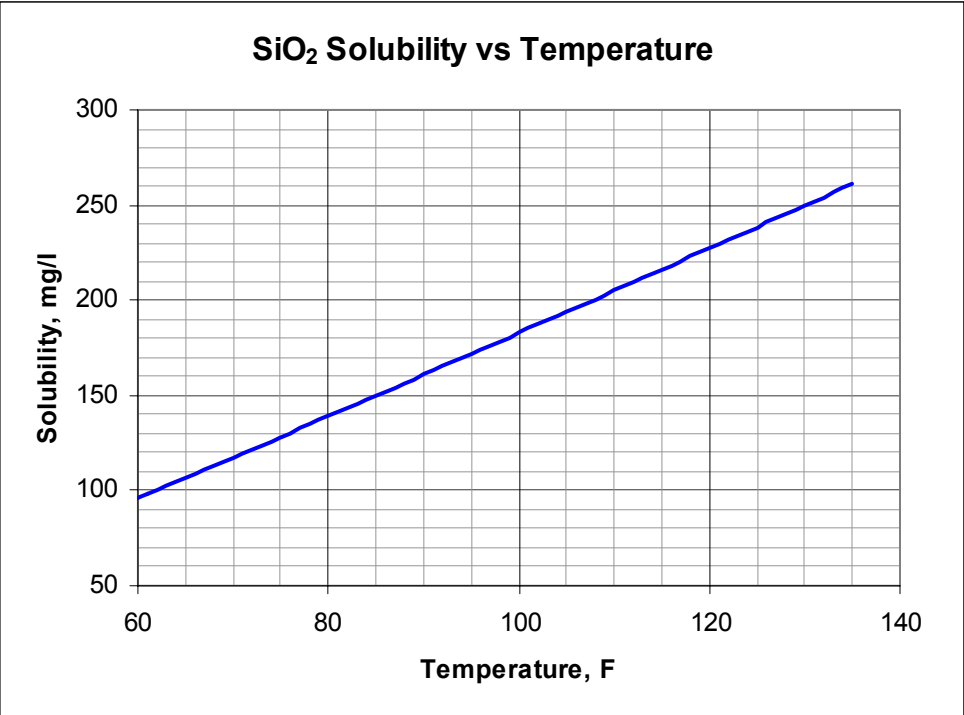


**Figure 7-17.**

Transfer values for  $\text{SiO}_2$  from Table 7-1 and activity concentrations for  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{OH}^{-1}$ ,  $\text{CO}_3^{-2}$ ,  $\text{SO}_4^{-2}$ ,  $\text{HPO}_4^{-2}$ , and  $\text{PO}_4^{-3}$  from the Ion Activity Worksheet to Table 7-2. Calculate the activity product for the target scale-forming compounds. For a hot-side temperature of  $135^\circ\text{F}$  ( $57.2^\circ\text{C}$ ), determine the solubility product for  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ ,  $\text{CaHPO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$  found in Figures 7-13 through 7-16, respectively. Recall that these compounds are less soluble at higher temperatures. A temperature of  $135^\circ\text{F}$  ( $57.2^\circ\text{C}$ ) was chosen because it represents a worse-case operating condition for a cooling tower during hot summer conditions. For a cold-side temperature of  $70^\circ\text{F}$  ( $21^\circ\text{C}$ ), determine  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$  solubility from Figure 7-17.  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$  is less soluble at lower temperatures.

For silica solubility, assume a limit of 150 mg/l. This limit represents a broadly used convention that is a compromise between hot-side and cold-side temperatures typically seen in cooling systems. Refer to Figure 7-18. Using the assumed hot summer operating condition ( $135^\circ\text{F}/57.2^\circ\text{C}$ ) as a worst-case operating example, silica solubility climbs to 255 mg/l. During the winter months, cold-side silica solubility could fall to less than 100 mg/l. Years of operating experience at a maximum silica concentration of 150 mg/l have proven that this limit is safe. Lastly, there are a number of relatively new silica threshold inhibitors available on the market, and many products are under development. These products claim to extend the silica solubility limit by 50%, to 225 mg/l.

Calculate the relative solubility of each target scaling component, as shown in Equation 49 and Table 7-2.



**Figure 7-18.**

**Table 7-2. Relative Solubility of Scale Forming Compounds**

		Units	Cycles of Concentration				
			4	6	8	10	12
Activity Concentrations (1)							
$A_{Ca^{+2}}$	A	mg/l <sub>Ca</sub>	34.5	43.1	50.7	55.6	61.6
$A_{Mg^{+2}}$	B	mg/l <sub>Mg</sub>	16.4	20.5	24.2	26.4	29.3
$A_{OH^{-1}}$	C	mg/l <sub>OH</sub>	0.011	0.011	0.011	0.011	0.011
$A_{CO_3^{-2}}$	D	mg/l <sub>CO3</sub>	0.018	0.017	0.019	0.019	0.018
$A_{SO_4^{-2}}$	E	mg/l <sub>SO4</sub>	447.2	602.2	737.7	839.7	968.2
$A_{HPO_4^{-2}}$	F	mg/l <sub>HPO4</sub>	7.26	10.2	13.1	15.4	18.2
$A_{PO_3^{-3}}$	G	mg/l <sub>PO4</sub>	0.00011	0.00014	0.00019	0.00023	0.00025
SiO <sub>2</sub> (2)	H	mg/l <sub>SiO2</sub>	64	96	128	160	192
Activity Products for Scale-Forming Compounds							
$A_{Ca^{+2}} \times A_{CO_3^{-2}}$	J=AxD	mg/l <sup>2</sup>	0.62	0.73	0.96	1.06	1.11
$A_{Ca^{+2}} \times A_{SO_4^{-2}}$	K=AxE	mg/l <sup>2</sup>	15,428	25,955	37,401	46,687	59,641
$A_{Ca^{+2}} \times A_{HPO_4^{-2}}$	L=AxF	mg/l <sup>2</sup>	250	440	664	856	1,121
$(A_{Ca^{+2}})^3 \times (A_{PO_4^{-3}})^2$	M=A <sup>3</sup> xG <sup>2</sup>	mg/l <sup>5</sup>	0.00050	0.0016	0.0047	0.0091	0.0146
$(A_{Mg^{+2}})^2 \times (SiO_2)^3 \times (A_{OH^{-1}})^4$	N=B <sup>2</sup> xH <sup>3</sup> xC <sup>4</sup>	mg/l <sup>9</sup>	1.03	5.44	17.98	41.80	88.96
Solubility Products for Scale-Forming Compounds							
$K_{SP,CaCO_3}$	T = 135 F	mg/l <sup>2</sup>	4.5				
$K_{SP,CaSO_4}$	T = 135 F	mg/l <sup>2</sup>	51,500				
$K_{SP,CaHPO_4}$	T = 135 F	mg/l <sup>2</sup>	236				
$K_{SP,Ca_3(PO_4)_2}$	T = 135 F	mg/l <sup>5</sup>	5.7x10 <sup>-5</sup>				
$K_{SP,Mg_2Si_3O_8 \bullet 3.5H_2O}$	T = 70 F	mg/l <sup>9</sup>	0.52				
SiO <sub>2</sub> Solubility	-----	mg/l	150				

(Table 7-2 is continued on the next page)

**Table 7-2 (continued)**

Units	Cycles of Concentration				
	4	6	8	10	12

**Relative Solubility for Scale-Forming Compounds**

$RS_{CaCO_3}$	$J \div K_{SP, CaCO_3}$	0.14	0.16	0.21	0.23	0.25
$RS_{CaSO_4}$	$K \div K_{SP, CaSO_4}$	0.30	0.50	0.73	0.91	1.16
$RS_{CaHPO_4}$	$L \div K_{SP, CaHPO_4}$	1.06	1.86	2.81	3.63	4.75
$RS_{Ca_3(PO_4)_2}$	$M \div K_{SP, Ca_3(PO_4)_2}$	8.72	27.5	82.5	160	256
$RS_{Mg_2Si_3O_8 \cdot 3.5H_2O}$	$N \div K_{SP, Mg_2Si_3O_8 \cdot 3.5H_2O}$	2.0	10.5	35	80	171
$RS_{SiO_2}$	$H \div 150$	0.43	0.64	0.85	1.07	1.28

**Notes**

1. Obtained from the Ion Activity Worksheet
2. Obtained from Table 7-1.

**7.3.5. Burden of Scale-Forming Compounds**

An estimate of the amount of scale-forming compounds in the cooling water (i.e., the burden) will be calculated for each compound. At saturation, the following relationship can be applied (calcium carbonate will be used as an example):

$$K_{SP, CaCO_3} = A_{Ca^{+2}} A_{CO_3^{-2}} \quad (50)$$

When saturation is exceeded.

$$K_{SP, CaCO_3} < A_{Ca^{+2}} A_{CO_3^{-2}} \quad (51)$$

Saturation is achieved at equilibrium as excess ions combine to form the insoluble salt. In this case,  $x$  moles per liter of  $CaCO_3$  are formed to achieve saturation as follows:

$$K_{SP, CaCO_3} = (A_{Ca^{+2}} - x)(A_{CO_3^{-2}} - x) \quad (52)$$

Solving the quadratic expression for  $x$  yields:

$$x = \frac{A_{Ca^{+2}} + A_{CO_3^{-2}} - \sqrt{(A_{Ca^{+2}} + A_{CO_3^{-2}})^2 - 4(A_{Ca^{+2}} A_{CO_3^{-2}} - K_{SPCaCO_3})}}{2} \quad (53)$$

Equation 53 also applies to calculating the burden for calcium sulfate compounds (gypsum and anhydrate) and dicalcium phosphate.

For more complex relationships, such as calcium phosphate and magnesium silicate, approximations are employed. For calcium phosphate, the following holds:

$$K_{SP,Ca_3(PO_4)_2} = (A_{Ca^{+2}} - 3x)^3 (A_{PO_4^{-3}} - 2x)^2 \quad (54)$$

The solution for  $x$  is a trial and error solution—a fifth-order polynomial expression. An approximation is employed to simplify the solution. If we assume that  $A_{Ca^{+2}} \gg x$ , Equation 54 simplifies to:

$$K_{SP,Ca_3(PO_4)_2} \approx A_{Ca^{+2}}^3 (A_{PO_4^{-3}} - 2x)^2 \quad (55)$$

Solving for  $x$  yields:

$$x \approx \frac{A_{PO_4^{-3}} - \left\{ \frac{K_{SP,Ca_3(PO_4)_2}}{A_{Ca^{+2}}^3} \right\}^{1/2}}{2} \quad (56)$$

A similar analysis for  $Mg_2Si_3O_8 \cdot 3.5H_2O$ :

$$K_{SP,Mg_2Si_3O_8-3.5H_2O} = (A_{Mg^{+2}} - 2x)^2 ([SiO_2] - 3x)^3 (A_{OH^{-1}} - 4x)^4 \quad (57)$$

If we assume  $A_{Mg^{+2}} \gg x$  and  $[SiO_2] \gg x$ , then:

$$K_{SP,Mg_2Si_3O_8-3.5H_2O} = A_{Mg^{+2}}^2 [SiO_2]^3 (A_{OH^{-1}} - 4x)^4 \quad (58)$$

Solving for  $x$  yields:

$$x \approx \frac{A_{OH^{-1}} - \left\{ \frac{K_{SP, Mg_2Si_3O_8 \cdot 3.5H_2O}}{A_{Mg^{+2}}^2 [SiO_2]^3} \right\}^{1/4}}{4} \quad (59)$$

Lastly, silica burden is calculated by simply subtracting the silica solubility limit (150 mg/l<sub>SiO2</sub>) from the calculated concentration. Only subtraction is required, since there are no multi-ion interactions.

Transfer values for activity concentrations and solubility products from Table 7-2 into Table 7-3. Utilizing the derivations above, calculate the burden for each scale-forming compound. Note, when relative solubility is less than or equal to one, the compound is not saturated, or just saturated, and there will be no burden ( i.e., no scale is formed).

**Table 7-3. Burden of Scale-Forming Compounds**

		Units	Cycles of Concentration				
			4	6	8	10	12
Activity Concentrations (1)							
$A_{Ca^{+2}}$	A	mg/l <sub>Ca</sub>	34.5	43.1	50.7	55.6	61.6
$A_{Mg^{+2}}$	B	mg/l <sub>Mg</sub>	16.4	20.5	24.2	26.4	29.3
$A_{OH^{-1}}$	C	mg/l <sub>OH</sub>	0.011	0.011	0.011	0.011	0.011
$A_{CO_3^{-2}}$	D	mg/l <sub>CO3</sub>	0.018	0.017	0.019	0.019	0.018
$A_{SO_4^{-2}}$	E	mg/l <sub>SO4</sub>	447.2	602.2	737.7	839.7	968.2
$A_{HPO_4^{-2}}$	F	mg/l <sub>HPO4</sub>	7.26	10.2	13.1	15.4	18.2
$A_{PO_3^{-3}}$	G	mg/l <sub>PO4</sub>	0.00011	0.00014	0.00019	0.00023	0.00025
SiO <sub>2</sub> (2)	H	mg/l <sub>SiO2</sub>	64	96	128	160	192
Solubility Products for Scale-Forming Compounds (1)							
$K_{SP,CaCO_3}$	T = 135 F	mg/l <sup>2</sup>	4.5				
$K_{SP,CaSO_4}$	T = 135 F	mg/l <sup>2</sup>	51,500				
$K_{SP,CaHPO_4}$	T = 135 F	mg/l <sup>2</sup>	236				
$K_{SP,Ca_3(PO_4)_2}$	T = 135 F	mg/l <sup>5</sup>	5.7x10 <sup>-5</sup>				
$K_{SP,Mg_2Si_3O_8 \bullet 3.5H_2O}$	T = 70 F	mg/l <sup>9</sup>	0.52				
SiO <sub>2</sub> Solubility	-----	mg/l	150				
Burden of Scale-Forming Compounds							
CaCO <sub>3</sub>	(Note 2)	mg/l	0	0	0	0	0
CaSO <sub>4</sub>	(Note 2)	mg/l	0	0	0	0	7.97
CaHPO <sub>4</sub>	(Note 2)	mg/l	0.35	4.14	7.62	10.2	13.3
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	(Note 2)	mg/l	3.64x10 <sup>-5</sup>	5.67x10 <sup>-5</sup>	8.45x10 <sup>-5</sup>	1.06x10 <sup>-4</sup>	1.17x10 <sup>-4</sup>
Mg <sub>2</sub> Si <sub>3</sub> O <sub>8</sub> •3.5H <sub>2</sub> O	(Note 2)	mg/l	4.33x10 <sup>-4</sup>	0.00122	0.00161	0.00183	0.00199
SiO <sub>2</sub>	150-H	mg/l	0	0	0	10	42
Notes							
1. Obtained from Table 7-2.							
2. Refer to Equation 53 for CaCO <sub>3</sub> , CaSO <sub>4</sub> , and CaHPO <sub>4</sub> ; Equation 56 for Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ; and Equation 59 for Mg <sub>2</sub> Si <sub>3</sub> O <sub>8</sub> •3.5H <sub>2</sub> O.							

#### 7.4. Summarizing the Data

The data found in Table 7-4 is a compilation of the calculations performed to this point. Table 7-4 summarizes relative solubility and burden concentrations for the scaling compounds of concern for five cycles-of-concentration scenarios. Scaling compounds are highlighted at cycles of concentration where relative saturation is exceeded. Highlighting is also applied to the corresponding burden concentrations.

**Table 7-4. Data Summary**

	Units	Cycles of Concentration				
		4	6	8	10	12
Cooling Tower Parameters (1)						
pH	----	7.0	7.0	7.0	7.0	7.0
Adjusted TDS <sub>Ion</sub>	mg/l	2,293	3,380	4,469	5,539	6,593
Relative Solubility for Scale-Forming Compounds (2)						
$RS_{CaCO_3}$	mg/l <sub>OH</sub>	0.14	0.16	0.21	0.23	0.25
$RS_{CaSO_4}$	mg/l <sub>CO3</sub>	0.30	0.50	0.73	0.91	1.16
$RS_{CaHPO_4}$	mg/l <sub>SO4</sub>	1.06	1.86	2.81	3.63	4.75
$RS_{Ca_3(PO_4)_2}$	mg/l <sub>HPO4</sub>	8.72	27.5	82.5	160	256
$RS_{Mg_2Si_3O_8 \bullet 3.5H_2O}$	mg/l <sub>PO4</sub>	2.0	10.5	35	80	171
$RS_{SiO_2}$	mg/l <sub>SiO2</sub>	0.43	0.64	0.85	1.07	1.28
Burden of Scale-Forming Compounds (3)						
CaCO <sub>3</sub>	mg/l	0	0	0	0	0
CaSO <sub>4</sub>	mg/l	0	0	0	0	7.97
CaHPO <sub>4</sub>	mg/l	0.35	4.14	7.62	10.2	13.3
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	mg/l	3.64x10 <sup>-5</sup>	5.67x10 <sup>-5</sup>	8.45x10 <sup>-5</sup>	1.06x10 <sup>-4</sup>	1.17x10 <sup>-4</sup>
Mg <sub>2</sub> Si <sub>3</sub> O <sub>8</sub> •3.5H <sub>2</sub> O	mg/l	4.33x10 <sup>-4</sup>	0.00122	0.00161	0.00183	0.00199
SiO <sub>2</sub>	mg/l	0	0	0	10	42
Notes						
1. Obtained from Ion Activity Worksheet.						
2. Obtained from Table 7-2.						
3. Obtained from Table 7-3.						

Reviewing the data shows that two scaling-forming components appear to be of immediate concern—Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O. The relative solubility of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, which is 8.72 (times its saturation limit) at only 4 cycles of concentration, is noteworthy, but not unusual for treated municipal effluent. The relative saturation for Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O is 2.0 at 4 cycles as well. CaHPO<sub>4</sub> just exceeds saturation at 4 cycles of concentration. SiO<sub>2</sub> and CaSO<sub>4</sub> are above saturation at 10 and 12 cycles of concentration, respectively.

To place the relative saturation levels of these salts into perspective, refer to the burden created by the scale-forming compounds in Table 7-4. Recall that burden is the estimated amount of



scale formed (insoluble salt expressed as mg/l) in the cooling water. Even though  $\text{Ca}_3(\text{PO}_4)_2$  is at 8.72 times saturation, the estimate of its burden is only  $3.64 \times 10^{-5}$  mg/l at 4 cycles of concentration (equivalent to a concentration of 0.036 parts per billion). For  $\text{Ca}_3(\text{PO}_4)_2$ , relative solubility varies with the cube of the calcium concentration and the square of the phosphate concentration. Therefore, small changes in their concentrations can greatly magnify relative solubility. For example, as the calcium and phosphate levels increase with cycles of concentration, the relative solubility of  $\text{Ca}_3(\text{PO}_4)_2$  changes dramatically (e.g., relative solubility increases to 27.5 at 6 cycles and to 82.5 at 8 cycles). This magnifying effect can also be applied to  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$ . The burden of  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$  at 4 cycles of concentration is only 0.00043 mg/l.

For the one-to-one ion-paired salts like  $\text{CaCO}_3$ ,  $\text{CaSO}_4$ , and  $\text{CaHPO}_4$ , burden is more significant at saturation. Note the burden concentrations of  $\text{CaSO}_4$  and  $\text{CaHPO}_4$  when relative saturation is just exceeded (i.e., 7.97 mg/l and 0.35 mg/l, respectively). For silica, the burden is equivalent to the difference between the cycled concentration and the silica limit—10 mg/l of burden at 10 cycles.

Relative saturation is a good indicator of when salts are likely to precipitate; however, burden quantifies the amount of salt formation in the cooling system. *Neither indicator can predict the behavior of the salts in the cooling water, i.e. how much of which salt will deposit on heat transfer surfaces as scale.*

## **7.5. Comparing Results to Indices and Standards**

The detailed analysis of the sample water at this point in the report is complete and will be compared to the simple indices and guidelines widely used to evaluate candidate cooling waters. Table 7-5 presents the results of analyzing the sample water using simple indices and guidelines. Guidelines (which were developed by EPRI in 1982 and updated in 1998) are found in Table 2-1 and were used to perform this analysis. Table 7-5 also includes the relative saturation results from the data summary in Table 7-4 for comparative purposes. Only three parameters are evaluated using the indices and guidelines— $\text{CaCO}_3$ ,  $\text{CaSO}_4$ , and  $\text{Mg}_2\text{Si}_3\text{O}_8$ . Phosphate salts were not evaluated, because no specific guidelines are offered in Table 2-1.

The guidelines overstate  $\text{CaCO}_3$  and  $\text{CaSO}_4$  solubility. The Langelier Saturation Index for  $\text{CaCO}_3$  and the  $\text{CaSO}_4$  guideline predict scale formation at 8 cycles of concentration and above for both salts. The Ryznar Stability Index, in contrast, predicts no scale formation in any of the cycles-of-concentration scenarios (the Ryznar Index is a derivative of the Langelier Index (see Section 2, Indices and Guidelines)). In contrast, the site-specific analysis performed in this section predicts no scale formation for  $\text{CaCO}_3$  through 12 cycles and scale formation for  $\text{CaSO}_4$  at 12 cycles. This difference between using a guideline and performing a rigorous site-specific analysis points to the adjustments made for calcium and sulfate ion associations. These differences are significant because the burden that results from mono-paired salts can be significant even at low relative solubility. Also, the sample water could be utilized more efficiently (generating less blowdown from the cooling tower) at higher cycles of concentration.

The guidelines understate  $\text{Mg}_2\text{Si}_3\text{O}_8$  solubility. The solubility of  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$  (sepiolite) is approximated by the  $\text{Mg}_2\text{Si}_3\text{O}_8$  guideline. The guidelines predict that saturation is exceeded at 6 cycles of concentration. The detailed analysis predicts saturation is exceeded at 4 cycles. Even though the problem is understated, the sepiolite burden should be quite low.

As stated above, there are no guidelines for phosphate salts of formation. As can be seen in Table 7-5, the solubility of both calcium phosphate salts is exceeded and the burden from  $\text{CaHPO}_4$  is noteworthy. Without this type of detailed analysis, phosphates cannot be evaluated. A rule of thumb used by many power plant developers for reclaimed municipal effluent (e.g., source waters containing orthophosphate) is to operate the cooling tower at a pH of 6.8 to 7.2 and stay below 4 to 5 cycles of concentration. This rule of thumb is fine for coastal plants where blowdown can usually be returned to the municipal treatment plant. It is unworkable (and costly) at inland plants where excessive cooling tower blowdown from operating at low cycles of concentration is usually treated via zero liquid discharge equipment, i.e. evaporator and crystallizers. As discussed later in this section of the report, this water will be usable in a power plant cooling tower at 8 cycles of concentration with a dramatic reduction in wastewater generation as compared to 4 cycles—approximately 60% less blowdown.

The guidelines state that ammonia must be kept under 2 mg/l in the cooling water. This rule only applies if any of the metallurgy of the cooling water system contains certain copper-bearing alloys, e.g., admiralty brass or silicon bronze. Ammonia is a primary constituent in municipal effluent. Some treatment plants nitrify their wastewater (convert the ammonia to nitrates), but this type of treatment is an exception. Many power plant developers using municipal effluent will use titanium for the condenser tubes and stainless steel fittings in the cooling system structure to avoid this problem, and therefore, can ignore the ammonia rule. Acceptable alloys in the presence of ammonia include carbon steel, stainless steel (304, 316, or 316L), titanium, and copper-nickel alloys (90-10 or 7-30). Lastly, ammonia creates other problems. It readily reacts/interferes with halogen-based biocides to form chloramines and bromamines (bromamines are unstable and revert back to active free-halogen form). When ammonia is present, halogen consumption is increased. Ammonia is also a nutrient source for bacteria. In extreme cases, it can encourage the growth of nitrifying bacteria, which convert ammonia to nitrate—a problem in some receiving waters.

Other parameters, such as iron (Fe), manganese (Mn), copper (Cu), aluminum (Al), and sulfide (S) are presented in Table 2-1 but were not evaluated in this section. These are usually trace constituents and should be addressed fully when a detailed water quality analysis is obtained; the guidelines in Table 2-1 are generally accepted for this purpose. Most of these constituents are found in fresh and degraded waters. Iron, copper, and aluminum can also be generated as products of corrosion in the cooling system.

**Table 7-5. Site-Specific Analysis Comparisons to Indices and Guidelines**

	Units	Cycles of Concentration				
		4	6	8	10	12
Simple Indices and Guidelines						
pH	----	7.0	7.0	7.0	7.0	7.0
TDS (1)	mg/l	2,657	3,982	5,309	6,635	7,961
Total Ca <sup>+2</sup> (2)	mg/l <sub>CaCO3</sub>	326.0	489.0	652.0	815.0	978.0
Total Mg <sup>+2</sup> (2)	mg/l <sub>CaCO3</sub>	255.4	383.2	510.9	638.6	766.3
M Alkalinity (3)	mg/l <sub>CaCO3</sub>	47	47	47	47	47
Total SO <sub>4</sub> <sup>-2</sup> (3)	mg/l	1,239.6	1,881.9	2,523.8	3,166.3	3,808.8
Ortho-PO <sub>4</sub> (9)	mg/l	23.6	35.4	47.2	59.1	70.8
pH <sub>S</sub> (4,5)	----	7.26	7.10	6.99	6.90	6.83
Langelier Saturation Index (4,5)	----	-0.26	-0.10	0.01	0.10	0.17
Ryznar Stability Index (4,5)	----	7.52	7.20	6.98	6.80	6.66
Ca x SO <sub>4</sub> (2,3,7)	mg/l <sup>2</sup>	162,000	368,000	658,000	1,032,000	1,490,000
Mg x SiO <sub>2</sub>	(Note 8)	16,300	36,800	65,400	102,200	147,100
RS <sub>CaCO<sub>3</sub></sub> (6)	----	0.55	0.79	1.02	1.25	1.48
RS <sub>CaSO<sub>4</sub></sub> (10)	----	0.32	0.74	1.32	2.06	2.98
RS <sub>Mg x SiO<sub>2</sub></sub> (10)	----	0.47	1.05	1.87	2.92	4.20
Relative Solubility for Scale-Forming Compounds: Site-Specific Analysis (2)						
RS <sub>CaCO<sub>3</sub></sub>	mg/l <sub>OH</sub>	0.14	0.16	0.21	0.23	0.25
RS <sub>CaSO<sub>4</sub></sub>	mg/l <sub>CO3</sub>	0.30	0.50	0.73	0.91	1.16
RS <sub>CaHPO<sub>4</sub></sub>	mg/l <sub>SO4</sub>	1.06	1.86	2.81	3.63	4.75
RS <sub>Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub></sub>	mg/l <sub>HPO4</sub>	8.72	27.5	82.5	160	256
RS <sub>Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O</sub>	mg/l <sub>PO4</sub>	2.0	10.5	35	80	171
RS <sub>SiO<sub>2</sub></sub>	mg/l <sub>SiO2</sub>	0.43	0.64	0.85	1.07	1.28
Notes						
1.	Obtained from Table 7-1 (sum of all ionic and soluble constituents except volatiles).					
2.	Obtained from Ion Association Worksheet.					
3.	Obtained from Sulfate Calculation Worksheet.					
4.	Refer to Equations 1 through 4 in Section 2, Indices and Guidelines.					
5.	Cooling tower hot-side temperature is 135°F (57.2°C).					
6.	LSI Relative Saturation is the degree of saturation of CaCO <sub>3</sub> calculated as 10 <sup>LSI</sup> .					
7.	Ca <sup>+2</sup> converted from mg/l <sub>CaCO3</sub> to mg/l <sub>Ca</sub> in this calculation. Refer to Table 6-1.					
8.	Mg <sup>+2</sup> expressed as mg/l <sub>CaCO3</sub> and SiO <sub>2</sub> as mg/l <sub>SiO2</sub> .					
9.	Sum of the Ortho-PO <sub>4</sub> species found in Table 7-1 – H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup> , HPO <sub>4</sub> <sup>-2</sup> , and PO <sub>4</sub> <sup>-3</sup> .					
10.	The solubility products for CaSO <sub>4</sub> and Mg <sub>2</sub> SiO <sub>4</sub> are 500,000 and 35,000, respectively. Constants were obtained from Table 2-1.					

## 7.6. Interpreting the Results

When reviewing the results of the site-specific analysis just performed, focus needs to be placed on two parameters—relative saturation, and burden concentration of scale-forming salts—to determine a safe operating point for the cooling tower. Relative saturation will identify those salts that are in excess of saturation and likely to form scaling salts. Burden will identify the concentration of salts formed in solution. Neither will predict the degree of scale formation on heat transfer surfaces.

As summarized in Table 7-4, five scaling constituents are likely to form when operating the cooling tower from 4 to 12 cycles of concentration. Relative saturation for  $\text{CaHPO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , and  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$  is exceeded at 4 cycles, saturation is exceeded for  $\text{SiO}_2$  at 10 cycles and  $\text{CaSO}_4$  at 12 cycles. At first glance, it appears that the cooling tower should be operated at 4 cycles of concentration, to avoid scaling problems with  $\text{CaHPO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$ . However, the burden concentrations for  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$  are very low, and the burden for  $\text{CaHPO}_4$  is moderate.

As discussed in Section 5, Specialty Chemicals, a threshold inhibitor will be required to interfere with crystal growth of the scale-forming salt and a dispersant to keep salt crystals in suspension in the bulk cooling water. This treatment approach also encourages the formation of soft scale in low-flow/stagnant areas of the cooling system—soft scale is easily removed. There are cooling systems that employ threshold inhibitors and dispersants that operate with burden/suspended matter levels approaching 200 to 300 mg/l. Consequently, the burden created by  $\text{CaHPO}_4$ ,  $\text{Ca}_3(\text{PO}_4)_2$ , and  $\text{Mg}_2\text{Si}_3\text{O}_8 \cdot 3.5\text{H}_2\text{O}$  at 4 cycles of concentration is negligible. Actually, the cooling system could be operated safely at a pH of 7.0 at 8 cycles of concentration (just below the  $\text{SiO}_2$  operating limit) and the scale-forming salt burden would be less than 10 mg/l. Also, because this water requires operating the cooling system at a relatively low pH, corrosion could be a problem if there are wetted carbon-steel surfaces. In this case, polyphosphates would have to be added to the cooling tower for corrosion protection. Therefore, some level of phosphate burden is preferable.

To complete this analysis as described in Figure 7-1, the pH should be varied to select an optimal/safe operating range for cycles of concentration and pH. This would be cumbersome using the methodology presented in this section of the report. The spreadsheet calculator was developed specifically for this purpose and will be discussed in Section 8.

## 8.0 Water Quality Calculator

### 8.1. Introduction

A water quality calculator was developed to assess cooling water chemistry using the source water evaluation methodology set forth in the previous sections. The calculator allows the user to quickly assess the potential of source waters for cooling tower application. It also eliminates common hand-calculation and chart-reading errors, especially those that occur early in an assessment and carry through the entire evaluation.

The assessment tool is designed to perform calculations required to:

- balance and speciate source water chemistry, and
- evaluate cooling tower saturation chemistry for common scaling compounds at various pH and temperature operating scenarios.

The calculator is in an Excel spreadsheet and performs all of the calculations found in Section 6, Source Water Chemistry, and Section 7, Sight-Specific Analysis.

### 8.2. Loading the Water Quality Calculator

The water quality calculator (WQ calculator) is an Excel spreadsheet (CEC-500-2005-170.XLS), and as such, it can be loaded as a spreadsheet file. Also, it may be helpful to create a shortcut on the desktop to more easily access the spreadsheet. Note that the WQ calculator contains example data discussed in this report. To use the spreadsheet for specific source water analyses, users should save it as a template, rename it as applicable for each particular analysis, and replace the example data with their own site-specific data. To download the calculator, [click here](#).

### 8.3. Spreadsheet Arrangement

The water quality calculator is a spreadsheet program consisting of one input sheet and six output sheets. The Input worksheet (Data Input) is used to enter the chemistry of the source water and operating characteristics of the cooling tower—namely pH, and hot-side and cold-side cooling water temperature. Acceptable data ranges are identified for each entry. If an entry is outside the acceptable range or entered incorrectly, a default value will be substituted and used for calculation purposes.

The six output worksheets are provided in the following order:

- Bal-Spec Source is a table that shows the results of balancing and speciating source water data.
- Analysis Summary is a table that summarizes the cooling tower chemistry, ion associations and relative saturation and burden concentrations for scaling salts.
- Relative Saturation is a chart that shows the relative saturation for scaling compounds for the complete range of cycles of concentration.
- Ca Salts-SiO<sub>2</sub> Burden is a chart that shows the burden concentrations for CaCO<sub>3</sub>, CaSO<sub>4</sub>, CaHPO<sub>4</sub>, and SiO<sub>2</sub>.
- Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O Burden is a chart that shows the burden concentrations for Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O.

- Total Burden-SiO<sub>2</sub>-LSI is a summary chart that shows the total burden concentration for the scaling salts, as well as SiO<sub>2</sub> relative saturation and adjusted LSI.

#### 8.4. Entering Data

Open the WQ calculator and copy it as a file with a different name (use the Excel “File/Save As” commands). This will preserve the master file and will allow the new file to be designated with a site-specific name (e.g., MuniEff-XYZpowerplant.xls). Page to the Data Input worksheet and enter source water and cooling tower operating data as instructed. Refer to Table 8-1. Data should be entered in the pink-colored boxes only. The top left of the input data sheet has spaces for the name of the source water, project name and date. Representations of all tables and graphs are placed at the end of this section to more easily follow spreadsheet sequencing.

Acceptable data ranges and default conditions are provided to the far right of the input sheet in the yellow highlighted area. If an entry is outside an acceptable range or entered incorrectly, a default value will be substituted and used for calculation purposes. Also, a message will be displayed in the Default Summary (e.g., “Default Cooling Tower pH”) along with the preset default value. Refer to Table 8-2. A “no-default” condition or acceptable data-entry will be designated as “N/A” (not applicable) in the default summary. Defaults are designed to filter and correct improperly entered data to protect the spreadsheet.

#### 8.5. Data Output

The six data output worksheets are provided in two formats—tabular and graphical. The first two are tables, and the remaining four are charts. These are presented in their order of appearance:

1. Bal-Spec Source shows the results of balancing and speciating the source water data. Note that a variance calculation is performed to assess source water electroneutrality—the ratio of cation to anion charge. Recall that the charge ratio should be within 0.9 to 1.1. Significant variances to this range could mean there is a problem with the source water data. Refer to Table 8-3. Balanced and speciated data is used to execute all calculations in the spreadsheet.
2. Analysis Summary presents cooling tower chemistry and ion associations, and relative saturation and burden concentrations for scaling salts. The analysis also includes comparative Langelier Saturation Indices (LSI) with and without adjustments for ionic strength and ion association. In addition to CaSO<sub>4</sub><sup>0</sup> and MgSO<sub>4</sub><sup>0</sup> calculated in the previous section of the report, association concentrations are also calculated for NaSO<sub>4</sub><sup>-1</sup>, KSO<sub>4</sub><sup>-1</sup>, and NH<sub>4</sub>SO<sub>4</sub><sup>-1</sup>. Saturation and burden calculations are provided for CaCO<sub>3</sub>, CaSO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, CaHPO<sub>4</sub>, Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O, and SiO<sub>2</sub>. Calculations are provided for a range of cycles of concentration from 4 to 20 in one-cycle increments (4, 5, 6, etc.). Refer to Table 8-4. As will be discussed later, cooling tower pH and temperature (as well as possible seasonal changes in water quality) can be adjusted to determine their affects on relative saturation and burden concentration.
3. Relative Saturation shows the relative saturation for each scaling compound for the complete range of cycles of concentration (4 to 20). A logarithmic scale is used to depict saturation relationships because all scaling salts can be presented in one chart. It also permits grossly oversaturated salts to be easily identified. Refer to Figure 8-1.

4. Ca Salts-SiO<sub>2</sub> Burden shows the burden concentration for CaCO<sub>3</sub>, CaSO<sub>4</sub>, CaHPO<sub>4</sub>, and SiO<sub>2</sub>. The burden for these salts can be relatively large (from 1 to 100 mg/l) when saturated, so they are grouped together in one chart for comparative purposes. Refer to Figure 8-2.
5. Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O Burden shows the burden concentration for Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O. The burden for these salts can be relatively small (0.0001 to 1 mg/l) when saturated, so they are also grouped together. Refer to Figure 8-3.
6. Total Burden-SiO<sub>2</sub>-LSI is a summary chart that shows the total burden for the scaling species identified above, as well as SiO<sub>2</sub> relative saturation and LSI (adjusted for ion association and ion strength). Refer to Figure 8-4. This chart is useful because it presents an overview of predicted cooling tower operating conditions for a given set of input assumptions.

## 8.6. Using the Water Quality Calculator

The pH used in the analysis is critical to obtaining reasonable results. When analyzing source waters with significant levels (greater than 0.3 mg/l<sub>P</sub>) of orthophosphate, such as municipal effluent or agricultural runoff, start with a pH of 7.0. Start with a pH of 8.0 for source waters with lower concentrations of orthophosphate. For temperature selection, use typical summer-day design conditions. Worst case hottest-day conditions may only occur eight hours during an entire year and could unnecessarily skew evaluation results and conclusions. In either case, the pH should be varied up or down to simulate the affects on relative saturation and total burden concentration of scaling salts. Start with variations of ±0.5 pH units and increase or decrease them depending on the results. Lastly, remember—the lower the pH, the greater the tendency for corrosion.

For degraded source water, it is likely that there will be saturation of one or more scaling salts. A total burden concentration of 100 mg/l should be considered a workable limit. This will allow for 100 to 200 mg/l of total suspended solids (TSS) from airborne particulate matter, for a total TSS of 300 mg/l. Cooling tower manufacturers will accept a 300 to 500 mg/l TSS limit with “non-foul” fill (specially designed for cooling water with high levels of TSS). *Note that with high levels of TSS, consistent and effective biological control is critical.* The combination of TSS and biological slimes can create significant soft-scale deposits on heat-transfer surfaces.

The Total Burden-SiO<sub>2</sub>-LSI worksheet should be used as a screening tool when varying cooling tower pH. It shows the total burden concentration, silica relative saturation, and adjusted LSI. As pH is varied, the total burden will change, therefore, the chart can be used to determine which criteria is limiting—total burden concentration or silica. If silica is clearly limiting, pH should be kept as high as possible to minimize corrosion. If burden is limiting, the worksheets Relative Saturation, Ca Salts-SiO<sub>2</sub> Burden, and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O Burden should be reviewed to determine which scaling salts are predominant, and to what degree. In some instances, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O burden concentrations will be less than 1 mg/l even though their relative saturations can exceed 1,000. Again, the key to deposit control when operating under scaling conditions is to maintain threshold inhibitor control and dispersant levels in the cooling water *at all times* (discussed in detail in Section 5, Specialty Chemicals). Lastly, some power plant operators try to keep Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> at relative saturation levels of less than 1,000, and LSI less than 2.0, regardless of burden concentrations.

### 8.7. Analysis of the Sample Source Water Data

The chemistry of the sample source water was carried forward from the previous two sections and entered into the WQ calculator. Refer to Table 8-1, the Data Input worksheet. There were no data entry errors (refer to Table 8-2); however, the speciated and balanced source water analysis showed that the cation/anion charge ratio was less than 0.9. This could mean there is a problem with the source water chemistry (which was not identified as a problem when hand calculated). Reviewing Figure 8-4, the Total Burden-SiO<sub>2</sub>-LSI output worksheet, it is clear that SiO<sub>2</sub> saturation is achieved at 9.5 cycles of concentration. Also, the total burden concentration at a cooling water pH of 7.5 and operating temperature of 135°F (57°C) is approximately 20 mg/l. The corrected LSI is approximately -0.5 (slightly corrosive conditions for carbon steel). Looking at Figure 8-2, the Ca Salts-SiO<sub>2</sub> Burden worksheet, most of the burden concentration is from CaHPO<sub>4</sub>. Figure 8-1, the Relative Saturation worksheet, shows that Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O are highly saturated, approximately 300 times and 100 times, respectively. However, in Figure 8-3, the Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O Burden worksheet, the burden concentrations of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O are approximately 0.0005 mg/l and 0.022 mg/l, respectively.

Given all these facts, SiO<sub>2</sub> is clearly the limiting constituent at 9.5 cycles of concentration. The burden concentration is relatively small, with the primary constituent being CaHPO<sub>4</sub>. At this point in the evaluation, focus should be placed on adjusting pH higher in the calculator to see how total burden concentration and the relative saturations of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>•3.5H<sub>2</sub>O are affected.

A treatment program should include a threshold scale inhibitor and dispersant. A dispersant with scale-inhibiting functions should work as well. If the cooling system has carbon steel wetted surfaces (this is not likely for a new plant), a polyphosphate should be used for corrosion protection. If the system has copper alloy, an azole corrosion inhibitor should be used.



Table 8-1. Example Data Input worksheetTable

Source Water Data Input

Source

Municipal Effluent

Project

XYZ Power

Date Entered

1/1/2003

Enter values in pink-colored boxes as applicable.  
Note range limitations and default conditions.

Red/bolded species must be entered

Species	Reported as	Reported Concentration	Concentration Units		Default Values	Default Conditions
<b>Sodium</b>	Na <sup>+1</sup>	116	mg/l as Na		10	No value, negative value
Potassium	K <sup>+1</sup>	12.5	mg/l as K		5	Negative value
<b>Calcium</b>	Ca <sup>+2</sup>	32.6	mg/l as Ca		10	No value, negative value
<b>Magnesium</b>	Mg <sup>+2</sup>	15.5	mg/l as Mg		10	No value, negative value
<b>M or Total Alkalinity</b>	CO <sub>2</sub> + HCO <sub>3</sub> <sup>-1</sup> + CO <sub>3</sub> <sup>-2</sup>	204	mg/l as CaCO <sub>3</sub>			
	HCO <sub>3</sub> <sup>-1</sup>		mg/l as CaCO <sub>3</sub>	Enter only one value	100 mg/l <sub>CaCO3</sub>	No value, negative value, multiple values
	HCO <sub>3</sub> <sup>-1</sup>		mg/l as HCO <sub>3</sub>			
<b>Chloride</b>	Cl <sup>-1</sup>	118	mg/l as Cl		10	No value, negative value
<b>Sulfate</b>	SO <sub>4</sub> <sup>-2</sup>	125	mg/l as SO <sub>4</sub>		10	No value, negative value
Nitrate	NO <sub>3</sub> <sup>-1</sup>	0.7	mg/l as N mg/l as NO <sub>3</sub>	Enter only one value	3 mg/l <sub>N</sub>	Negative value, multiple values
Nitrite	NO <sub>2</sub> <sup>-1</sup>	1.4	mg/l as N mg/l as NO <sub>3</sub>	Enter only one value	1 mg/l <sub>N</sub>	Negative value, multiple values
Ammonia	NH <sub>3</sub>	1.8	mg/l as N mg/l as NH <sub>3</sub>	Enter only one value	5 mg/l <sub>N</sub>	Negative value, multiple values
Ortho-Phosphate	H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup> , HPO <sub>4</sub> <sup>-2</sup> , PO <sub>4</sub> <sup>-3</sup>	1.9	mg/l as P mg/l as PO <sub>4</sub>	Enter only one value	1 mg/l <sub>P</sub>	Negative value, multiple values
<b>Silica</b>	SiO <sub>2</sub>	16	mg/l as SiO <sub>2</sub>		10	No value, negative value
<b>pH</b>		7.5	(Must be within range of 6.0 to 9.0)		7.5	Outside of range
Cooling Tower pH		7.0	(Must be within range of 6.0 to 9.0)		7.5	Outside of range
Hot-Side Cooling Tower Temperature, F		135	(Must be within range of 55 F to 135 F)		135	Outside of range
Cold-Side Cooling Tower Temperature, F		70	(Must be within range of 55 F to 135 F)		70	Outside of range

Data

**Table 8-2. Example of the “Default Summary” portion of the Data Input worksheet**

**Summary of Default Values Applied to Analysis**

Sodium	mg/l as Na	<i>N/A</i>
Potassium	mg/l as K	<i>N/A</i>
Calcium	mg/l as Ca	<i>N/A</i>
Magnesium	mg/l as Mg	<i>N/A</i>
M or Total Alkalinity	mg/l as CaCO <sub>3</sub>	<i>N/A</i>
Chloride	mg/l as Cl	<i>N/A</i>
Sulfate	mg/l as SO <sub>4</sub>	<i>N/A</i>
Nitrate	mg/l as N	<i>N/A</i>
Nitrite	mg/l as N	<i>N/A</i>
Ammonia	mg/l as N	<i>N/A</i>
Ortho-Phosphate	mg/l as P	<i>N/A</i>
Silica	mg/l as SiO <sub>2</sub>	<i>N/A</i>
pH		<i>N/A</i>
Cooling Tower pH		<i>N/A</i>
Hot-Side Cooling Tower Temperature, F		<i>N/A</i>
Cold-Side Cooling Tower Temperature, F		<i>N/A</i>

**Notes.....**

1. N/A = not applicable.

**Data Input**

**Table 8-3. Example Bal-Spec Source worksheet**

**Source Water - Speciated & Balanced**

<b>Source</b>	Municipal Effluent
<b>Project</b>	XYZ Power
<b>Date Entered</b>	1/1/2003

		<b>Reported</b>	<b>Speciated Balanced</b>
Na <sup>+1</sup>	mg/l	116	134.5937261
K <sup>+1</sup>	mg/l	12.5	12.5
Ca <sup>+2</sup>	mg/l	32.6	32.6
Mg <sup>+2</sup>	mg/l	15.5	15.5
NH <sub>4</sub> <sup>+1</sup>	mg/l		2.297311676
HCO <sub>3</sub> <sup>-1</sup>	mg/l		232.9242996
CO <sub>3</sub> <sup>-2</sup>	mg/l		0.213770537
Cl <sup>-1</sup>	mg/l	118	89.32651716
SO <sub>4</sub> <sup>-2</sup>	mg/l	125	125
NO <sub>3</sub> <sup>-1</sup>	mg/l	3.098650675	3.098650675
NO <sub>2</sub> <sup>-1</sup>	mg/l	4.5982009	4.5982009
H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup>	mg/l		1.520358795
HPO <sub>4</sub> <sup>-2</sup>	mg/l		4.382747184
PO <sub>4</sub> <sup>-3</sup>	mg/l		0.000149525
SiO <sub>2</sub>	mg/l	16	16
NH <sub>3</sub>	mg/l		0.019665338
H <sub>3</sub> PO <sub>4</sub>	mg/l		4.93419E-06
CO <sub>2</sub>	mg/l		11.08402642
pH	Std Units	7.5	7.5
TDS <sub>Ion</sub>	mg/l		668.6354888
Conductivity	μS/cm		940
TDS	mg/l		684.6354938
Water Temp (1)	F	60	60
Total Alkalinity	mg/l <sub>CaCO3</sub>	204	204
Total Ammonia	mg/l <sub>N</sub>	1.8	1.8
Ortho-Phosphate	mg/l <sub>P</sub>	1.9	1.9
Molar Electroneutrality		0.002187	0
Cation/Anion Charge Ratio		0.84	

*Source data problems may exist.  
High/low cation/anion charge ratio*

**Notes.....**

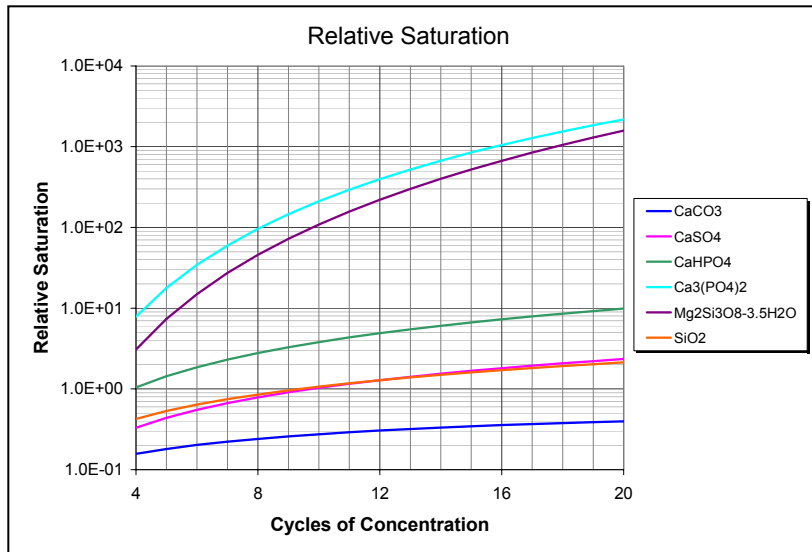
1. Assumed value - no data entry was required.

**Bal-Spec Source**

**Table 8-4. Example Analysis Summary worksheet**

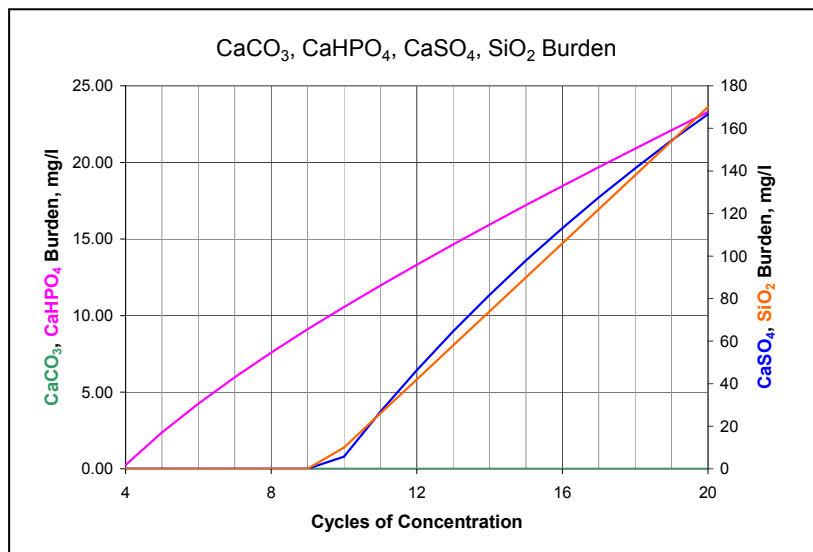
Cooling Tower Analysis Summary		partial view of worksheet					
Source	Municipal Effluent						
Project	XYZ Power						
Date Entered	1/1/2003						
		Speciated Balanced Source Water	Cooling Tower Cycles of Concentration				
			4	5	6	7	8
Free Na <sup>+1</sup>	mg/l	134.59	536.45	668.91	800.80	932.17	1,063.04
Free K <sup>+1</sup>	mg/l	12.50	49.81	62.23	74.64	87.04	99.43
Free Ca <sup>+2</sup>	mg/l	32.60	80.43	97.27	113.61	129.50	144.96
Free Mg <sup>+2</sup>	mg/l	15.50	39.05	47.28	55.27	63.05	70.62
Free NH <sub>4</sub> <sup>+1</sup>	mg/l	2.30	8.48	10.53	12.57	14.59	16.59
HCO <sub>3</sub> <sup>-1</sup>	mg/l	232.92	50.77	50.95	51.09	51.21	51.30
CO <sub>3</sub> <sup>-2</sup>	mg/l	0.21	0.04	0.04	0.04	0.04	0.05
Cl <sup>-1</sup>	mg/l	89.33	341.68	426.44	511.19	595.95	680.71
Free SO <sub>4</sub> <sup>-2</sup>	mg/l	125.00	974.39	1,206.42	1,433.81	1,656.95	1,876.09
NO <sub>3</sub> <sup>-1</sup>	mg/l	3.10	12.39	15.49	18.59	21.69	24.79
NO <sub>2</sub> <sup>-1</sup>	mg/l	4.60	18.39	22.99	27.59	32.19	36.79
H <sub>2</sub> PO <sub>4</sub> <sup>-1</sup>	mg/l	1.52	9.88	11.93	13.89	15.79	17.64
HPO <sub>4</sub> <sup>-2</sup>	mg/l	4.38	13.77	17.63	21.58	25.58	29.64
PO <sub>4</sub> <sup>-3</sup>	mg/l	1.495E-04	4.678E-04	6.549E-04	8.632E-04	1.090E-03	1.334E-03
NaSO <sub>4</sub> <sup>-1</sup>	mg/l		62.45	88.84	118.18	150.23	184.82
KSO <sub>4</sub> <sup>-1</sup>	mg/l		0.66	0.94	1.26	1.60	1.98
CaSO <sub>4</sub> <sup>0</sup>	mg/l		169.73	223.25	278.48	335.25	393.47
MgSO <sub>4</sub> <sup>0</sup>	mg/l		113.64	149.64	186.82	225.08	264.33
NH <sub>4</sub> SO <sub>4</sub> <sup>-1</sup>	mg/l		2.51	3.56	4.73	5.99	7.35
SiO <sub>2</sub>	mg/l	16.00	64.00	80.00	96.00	112.00	128.00
NH <sub>3</sub>	mg/l	0.02	0.37	0.47	0.56	0.65	0.75
H <sub>3</sub> PO <sub>4</sub>	mg/l	4.934E-06	1.294E-04	1.515E-04	1.722E-04	1.916E-04	2.102E-04
CO <sub>2</sub>	mg/l	11.08	4.93	4.81	4.70	4.61	4.54
pH	Std Units	7.50	7.00	7.00	7.00	7.00	7.00
TDS <sub>ion</sub>	mg/l	669	2,136	2,638	3,135	3,626	4,112
Conductivity (2)	µS/cm	940	2,990	3,690	4,390	5,080	5,760
TDS	mg/l	685	2,549	3,184	3,820	4,456	5,092
Water Temp (1)	F	60	135	135	135	135	135
Total Alkalinity (3)	mg/l <sub>CaCO3</sub>	204.00	47.32	47.32	47.32	47.32	47.32
Total Ammonia	mg/l <sub>N</sub>	1.80	7.20	9.00	10.80	12.60	14.40
Ortho-Phosphate	mg/l <sub>P</sub>	1.90	7.60	9.50	11.40	13.30	15.20
Langelier Saturation Index (LSI)			-0.22	-0.13	-0.06	0.00	0.05
LSI (with ion association)			-0.80	-0.74	-0.69	-0.65	-0.62
<b>Relative Saturation.....</b>							
CaCO <sub>3</sub>			0.16	0.18	0.20	0.22	0.24
CaSO <sub>4</sub>			0.33	0.44	0.55	0.67	0.79
CaHPO <sub>4</sub>			1.04	1.43	1.86	2.31	2.78
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>			7.882E+00	1.783E+01	3.450E+01	5.997E+01	9.645E+01
Cold-Side Mg <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> *3.5H <sub>2</sub> O			3.073E+00	7.360E+00	1.498E+01	2.728E+01	4.580E+01
SiO <sub>2</sub> (conventional guideline) (4)			0.43	0.53	0.64	0.75	0.85
<b>Burden Analysis.....</b>							
CaCO <sub>3</sub>	mg/l		0.00000	0.00000	0.00000	0.00000	0.00000
CaSO <sub>4</sub>	mg/l		0.00000	0.00000	0.00000	0.00000	0.00000
CaHPO <sub>4</sub>	mg/l		0.25347	2.36762	4.24976	5.97359	7.58285
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	mg/l		0.00010	0.00014	0.00018	0.00022	0.00026
Cold-Side Mg <sub>2</sub> Si <sub>2</sub> O <sub>7</sub> *3.5H <sub>2</sub> O	mg/l		0.01356	0.02145	0.02652	0.03002	0.03256
SiO <sub>2</sub> (conventional)	mg/l		0.00000	0.00000	0.00000	0.00000	0.00000
Total Burden	mg/l		0.26713	2.38922	4.27646	6.00383	7.61566

**Analysis Summary**



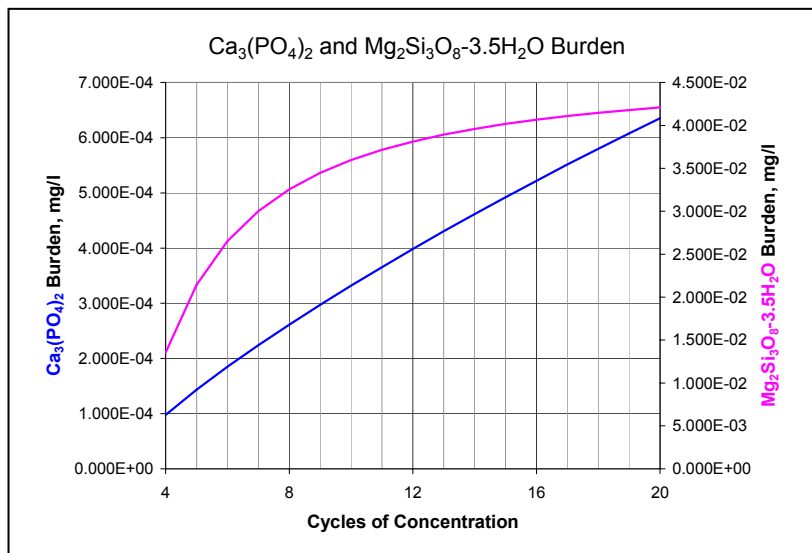
Relative Saturation

Figure 8-1. Example Relative Saturation worksheet



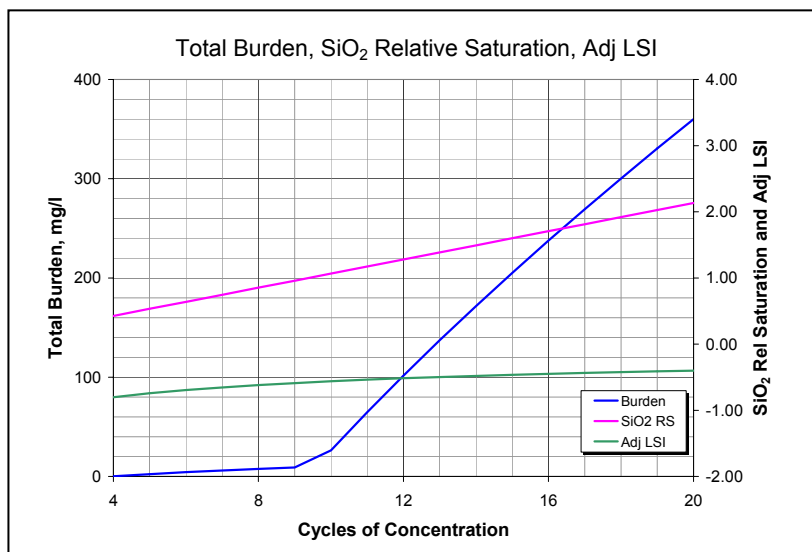
Ca Salts-SiO<sub>2</sub> Burden

Figure 8.2. Example Ca Salts-SiO<sub>2</sub> Burden worksheet



Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>-3.5H<sub>2</sub>O

Figure 8-3. Example Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> Mg<sub>2</sub>Si<sub>3</sub>O<sub>8</sub>-3.5H<sub>2</sub>O



Total Burden-SiO<sub>2</sub>-LSI

Figure 8-4. Example Total Burden-SiO<sub>2</sub>-LSI worksheet

## 9.0 References

- Ballard, C. W., and J. V. Matson. 1992. "Precise Prediction of Cooling Water pH." *Cooling Tower Institute Journal* 13 (1).
- Caplan, G. 1990. "Cooling Water Computer Calculations: Do They Compare?" *Corrosion 90 Proceedings*. Paper No. 100.
- Chmelovski, M. J. 1996. "Considerations for Understanding One's Cooling System Prior to Reuse Water Implementation." *Corrosion 96 Proceedings*. Paper No. 576.
- Dallmier, A. W., J. D. Martens, and W. F. McCoy. 1997. "Performance of Stabilized Halogen Biocides in Cooling Water." *Corrosion 97 Proceedings*. Paper No. 398.
- DiFilippo, M. N. 2002. "Use of Degraded Water Sources for Cooling Water in Power Plants." EPRI.
- Environmental Protection Agency. 2002. Federal Code of Regulations, Title 40, Chapter 1, Part 63, National Emissions Standard for Hazardous Air Pollutants for Source Categories (NESHAPS) for Source Categories, Subpart Q, NESHAPS for Industrial Process Cooling Towers (IPCT), Section 63.402.
- Ferguson, R. J., A. J. Freedman, G. Fowler, A. J. Kulik, J. Robson, D. J. Weintritt. 1994. "The Practical Application of Ion Association Model Saturation Level Indices to Commercial Water Treatment Problem Solving." *American Chemical Society National Meeting*.
- Hoots, J. E., D. A. Johnson, J. D. Lammering, D. A. Meier, B. Yang. 1999. "High Cycles Cooling Tower Operation: Hurdles and Solutions." *International Water Conference*. Paper No. IWC-99-48.
- Kunz, R. G., A.F. Yen, and T. C. Hess. 1977. "Cooling Water Calculations." *Chemical Engineering* (August) 61-71.
- Langelier, W. F. 1936. "The Analytical Control of Anti-Corrosion Water Treatment." *Journal AWWA* 28 (10):1500-1521.
- Lisin, M. A., and T. M. Laronge. 1993. "Pitting Corrosion of Cooling Water Systems." *CTI Journal* 22 (2).
- Micheletti, W. C., J. G. Noblett, Jr., K. A. Wilde. 1982. "Design and Operating Guidelines Manual for Cooling Water Treatment." EPRI.
- Puckorius, P. R., and G. R. Loretitsch. 1999. "Cooling Water Scale & Scaling Indices: What They Mean – How to Use Them – How They Can Cut Treatment Costs." *International Water Conference*. Paper No. IWC-99-47.
- Ryznar, J. W. 1944. "A New Index for Determining the Amount of Calcium Carbonate Scale Formed by a Water." *Journal AWWA* 36:472.
- Selby, K. A. 1998. "Cooling Water Treatment Manual." EPRI. (unpublished).
- Stumm, W., and J. J. Morgan. 1970. *Aquatic Chemistry*. Wiley-Interscience. 83-84.

Vanderpool, D. 1997. "New Calcium Carbonate Scale Inhibitors: Understanding Complexation Constants as a Tool for Finding Improved Performance." *International Water Conference*. Paper No. IWC-97-40.

"The Chemical Treatment of Cooling Water and the World Health Organization (Second Edition), Section A1, Polyphosphates", January 2001,  
<http://www.parafos.com/pages/deposition.html> .



## 10.0 Glossary

AMP	Aminomethylenephosphonic acid
AMPS	2-Acrylamido-2-methylpropanesulfonic Acid
BOD	biological oxygen demand
COD	chemical oxygen demand
HEDP	1-Hydroxyethylene-1,1-diphosphonic acid
LSI	Langelier Saturation Index
PAA	Polyacrylic acid
PBTC	2-Phosphonobutane-1,2,4-tricarboxylic acid
PMA	Polymaleic acid
PSI	Practical Scaling Index
RSI	Ryznar Stability Index
TDS	Total Dissolved Solids
TTA	Tolytriazoles